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A RECONNAISSANCE CLASSIFICATION OF THE SOILS OF THE SOUTH TURKANA DESERT

C. F. HEMMING

(*Desert Locust Survey*)

C. G. TRAPNELL

(*East African Agriculture and Forestry Research Organization*)

WITH EIGHT PLATES

Summary

Development of the Soil Pattern

As an outcome of an ecological reconnaissance this account provides a record of the occurrences of two major regional types, a system of consolidated sand dunes and derived sands, referred to here as the Chestnut Sands, and a wide assortment of stony truncated 'desert pavement' soils or soil remnants described as Stone Mantles. The latter involve areas both of basement complex and of lava origin. Briefer observations are also given on other soils of lesser extent, including flash-flood, alluvial and lacustrine deposits.

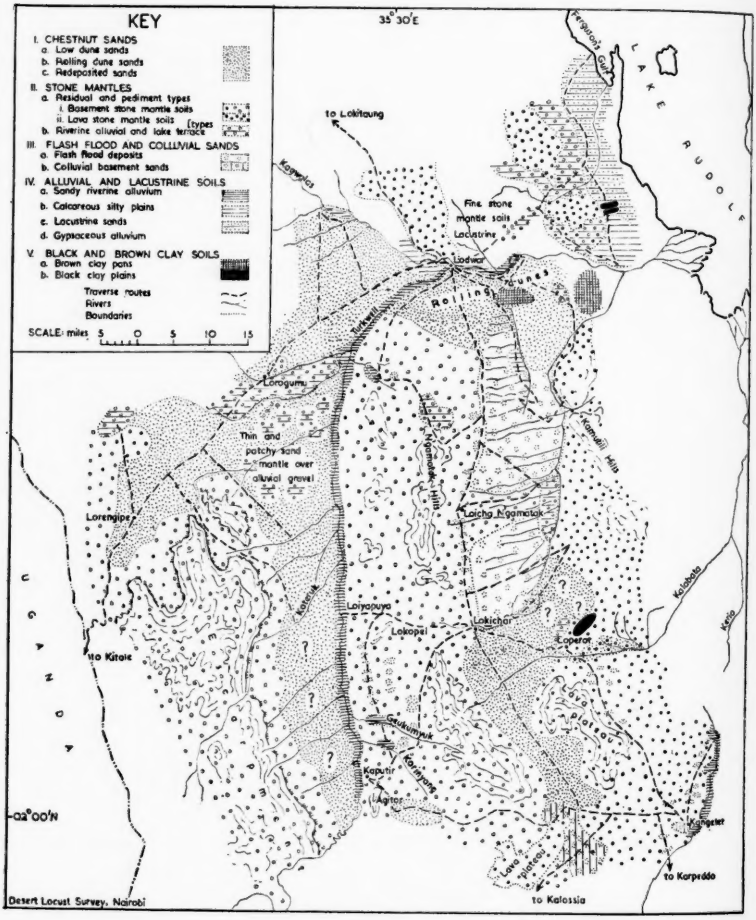
Although a present-day desert or semi-desert, the south Turkana region bears the stamp of successive erosion cycles, which have largely influenced its soil pattern. Modified remnants of the original end-Tertiary surface are probably discernible in the higher-lying stone mantles about the central hill ranges (Section 2, Introd.). Residual stone mantles of this class appear to be the last truncated remnants of an ancient soil cover. Ancient alluvial and lacustrine deposits, the former of conjectured and the latter of established Pleistocene age, have provided the material for other stone mantle areas (Section 2 (*b*)). The present surface of all these has been affected by more recent erosion and deflation.

On top of these several types of stone mantle, or the stony soils from which they originated, seems to have been deposited the deep mantle of the Chestnut Sands, blanketing at one time the greater part of the Turkana plain. These dune sands are regarded as a mainly aeolian drift, deposited during a period of active arid erosion, though their materials may have been derived from older surfaces (Section 1, Introd.). They must be subsequent to the deposits which they overlie, and may possibly be compared with the Goz or Kordofan Sands of the Sudan, which have been very tentatively referred to the late Pleistocene (Andrew, 1948).

As with the Goz Sands, the dunes of the Chestnut Sands presumably became fixed under less arid conditions. Finally, in common with the rest of the Turkana landscape, they have been subjected to the present régime of brief seasonal flash-flood erosion and intervening wind action. Their formerly extensive dune structure has been greatly modified and from many areas they appear to have been removed wholesale. The redeposited Chestnut Sands, the flash-flood deposits and sandy riverine alluvia are the outcome of this latest phase of erosion. At the same time tracts of comparatively recent lacustrine sands and possible deltaic silts (Section 4 (*b*)) have been left in the east of the region as a result of the progressive retreat of Lake Rudolf.

The influence of the resulting soil pattern on the vegetation of the region is very briefly indicated, with reference more particularly to the principal shrub components.

THIS account is intended to give a working field description of the soil pattern of the southern portion of the Turkana desert, lying between latitudes 3° 30′ N. and 2° N., and to convey a geographical picture of the distribution of the main types by means of a small-scaled sketch map.



The reconnaissance was carried out through an area of 6,000 square miles as part of a systematic investigation of the Desert Locust habitat, and took the form of continuous recorded traverse observations along the routes shown on the sketch map, with check hoe samplings at frequent intervals. The field work was followed by examination of available air photographs of the district. The results are those of a large-

scale reconnaissance rather than a full pedological investigation, and no more than a schematic map has been attempted having regard to the inadequate nature of the existing survey maps. A decidedly more detailed map would be possible, if it were warranted, in central and western portions of the region where air cover is available.

In attempting to deal with the whole surface of a desert area of this sort a difficulty frequently arises over the limits of the word soil. It must be understood that the word is here used in the widest sense as taking in any superficial deposit which shows traces of soil formation. Such phenomena as 'stone mantles' are commonly not soils in the accepted sense, or are at best their deflated remnants, but their great extent makes it essential to include them in the overall soil picture.

Topography and Geology

The Turkana desert is a distinct natural lowland area occupying the north-western corner of Kenya. The area is bounded in the north by the Sudan frontier, to the west by the Uganda escarpment, and to the east by Lake Rudolf. In the south it is bounded by Baringo and west Suk districts. The Turkana plain is about 90 miles in maximum width and about 200 miles long from north to south. The southern half of it, with which this paper is concerned, is in general flat with small hill ranges rising out of the plain. The southern end of the area lies at about 2,400 ft. and slopes northwards down to about 1,230 ft. where the River Turkwell enters Lake Rudolf. The general aspect is one of arid sand stretches and stone wastes with widely spaced thorny shrubs, traversed at intervals by ranges of abrupt stony hills. With the brief rains, however, the countryside is changed dramatically by the sudden flush of vegetation.

The latest account of the geology and geomorphology of the region is that of Dixey (1948). In contrast to north Turkana, which is largely occupied by volcanics, the greater part of the region considered here consists of ancient rocks of the basement complex, principally gneisses and schists. There are, however, large areas of lavas towards the east, notably in the Kamutili hills and in the lava-capped plateaux shown on the map to the south of them. These lavas—basalts and phonolites with interbedded sediments—are of Miocene age.

The Turkana plain is regarded by Dixey as a post-Miocene erosion surface, altered by later erosion cycles accompanying successive fluctuations in the level of Lake Rudolph. The original surface of the plain is held to have been of end-Tertiary or late Pliocene age, but this has been subject to subsequent modification. The formation of Lake Rudolph is attributed to gentle down-warping about the late Pliocene or early Pleistocene, with some minor faulting, traces of which are apparent in the aerial photographs of the region. In the mid-Pleistocene the lake rose to its highest level, at least 300 ft. above its present level, since when it has undergone successive retreats. The effects of these cycles and of the climatic changes which accompanied them have been of great importance in determining the soil pattern.

Climate

The average rainfall at Lodwar over 28 years is 5·7 in. In 1953 rain totalling 5·15 in. fell on 20 days, but both quantities and distribution are extremely variable. Champion (1937) records that during the period 1931–4 the rainfall was under 2 in. Vegetation changes indicate greatest aridity in the sector between Lodwar and Lake Rudolph, and an improvement towards Kaputir in the south (conjectured to touch 12 in. by Champion) and towards the foot of the Uganda escarpment south-west of Lorengipe. Temperatures are uniformly high and there is very little cooling at night. The mean daily maxima for the hottest and coolest months are 98·6° F. and 92·1° F. respectively, with the mean minima lying consistently at 74°. Strongish winds are frequent and persistent, and in flat areas sweep uninterrupted for many miles, carrying considerable quantities of dust and sand. Wind erosion is coupled with the effects of the few downpours, which tend to run off as flash floods through a maze of ephemeral watercourses.

The Soil Classes

The account of the soils follows the arrangement given below, this classification being used both in the text and the sketch map. The amount of detail given for each is roughly in proportion to their geographical extent.

1. *The Chestnut Sands*
   - (*a*) Low-dune sands.
   - (*b*) Rolling dune sands.
   - (*c*) Redeposited sands.

2. *Stone mantles and stone-mantle soils*
   - (*a*) Residual and pediment types.
     - (i) Basement stone mantles.
     - (ii) Lava stone mantles.
   - (*b*) Riverine alluvial and lake-terrace types.

3. *Flash-flood and colluvial sands*
   - (*a*) Flash-flood deposits.
   - (*b*) Colluvial basement sands.

4. *Alluvial and lacustrine soils*
   - (*a*) Sandy riverine alluvium.
   - (*b*) Calcareous silty plains.
   - (*c*) Lacustrine sands.
   - (*d*) Gypseous alluvium.

5. *Black- and brown-clay soils*
   - (*a*) Brown-clay pans.
   - (*b*) Black-clay plains.

1. *The Chestnut Sands*

The largest sectors of the Turkana plains are covered with a deep mantle of what are here termed chestnut sands. These sands vary from a slightly reddish chestnut to a duller rusty-brown colouring. They are compact sands of predominantly fine grain, but contain a small quantity of much coarser sand. This and the presence of undecomposed mineral fragments give them a finely mottled appearance. A mineralogical report by A. O. Thompson of the Kenya Mines and Geological Department states that the chief minerals present are quartz, hornblende, and mica. Rare grains of garnet, zircon, and iron ores are also present. The individual grains are abraded but not rounded. The sands are stated to have originated as a detrital eluvium from basement system rocks, derived under arid conditions with seasonal downpours, but widespread remnants of dune structure indicate that they must have been transported and spread over the valley floors chiefly by aeolian action. The characteristic colouring is due to rusty staining of the quartz grains. The lack of any minerals derived from the Tertiary lavas is noteworthy.

The chestnut sands are most extensively found in the form of low dunes with a covering of coarse loose sand. Below this they are strikingly cemented in the dry state, becoming almost like sandstone in the lower layers. Consequently, apart from superficial erosion, the dunes are now stable. Three categories of the sand are described: (*a*) the characteristic low-dune sands, (*b*) an area of much larger 'rolling' dunes and (*c*) redeposited sands derived from water erosion of the dune areas.

(*a*) *Low-dune sands*

The most typical areas of the chestnut sands consist of low dunes not usually more than about 6 ft. high, the distance between crests being very variable. Today these dunes, although in general stable, are in the process of being eroded away, both by wind and rain. Their surface is characteristically covered by a few inches of loose coarse rippled sand, which becomes deeper towards the crests. The coarse superficial layer is derived from the underlying sand by deflation, the smaller particles being blown away. The dune sides are often blown out on windward exposures, which are then devoid of loose sand and show a consolidated and cemented redder chestnut surface (Plate IIa). This surface has usually been fretted by the blowing sands. In some the dune crests are also devoid of the loose sand mantle and fretting at the top of the dune characteristically exposes many fine successive crust-like layers of compacted sand (Plate IIb).

In a typical site the dune crest showed a superficial layer of rippled coarse sand of light colouring—7·5 YR 6/4–6—overlying light chestnut-brown compacted sand—7·5 YR 5/6 in the first foot. A pit through the dune flank 15 ft. away showed:

0–12 in. Compacted, somewhat cemented chestnut sand—5 YR 4/6. Some slight vertical fissuring; slight lumpiness on cleavages.

12–18 in. Hard and cemented duller chestnut-brown sand—5 YR 4/4–7·5 YR 4/4.

18–36 in. Very hard cemented sand, of a dull somewhat ochreous brown colour—7·5 YR 4/4–5/6—giving a pale surface where sliced by the hoe. Small flecks of $CaCO_3$ present and increasing from 24 in. downwards.

The diminutive lime flecks, 1–2 mm. across, resemble 'pseudomycelia'. Distinct hard calcareous concretions are occasionally exposed at lower levels as a result of deflation. Apart from this the profile is little differentiated and is much less calcareous than some desert soils. The mechanical analysis is similar to that given by Jewitt for Goz sands in the Sudan (1950). Soluble sulphates in the dune flank profile were 139 p.p.m. below 24 in., increasing to 2760 p.p.m. at 6–12 in.; top horizon 275 p.p.m.

	Depth	*Coarse sand*	*Fine sand*	*Silt*	*Clay*	$CaCO_3$	*Soluble salts*	pH
Crest	Ripples	93·6	6·2	0	0	1·0	0·02	7·9
	0–6 in.	61·2	35·8	2·8	0	0·5	0·02	8·2
	6–12 in.	67·0	31·0	0·8	1·0	0	0·04	7·1
Flank	0–6 in.	48·3	43·5	0·9	7·1	0·7	0·22	9·6
	6–12 in.	56·0	35·8	2·9	5·1	1·0	0·33	8·6
	12–18 in.	42·1	49·7	1·8	6·1	1·0	0·24	8·8
	18–24 in.	46·9	44·9	3·9	4·1	0·7	0·14	9·3
	24–30 in.	46·3	45·1	4·1	4·3	1·0	0·18	9·9
	30–36 in.	40·7	51·2	3·8	4·1	1·0	0·18	9·9

The sands are remarkable for their property of reversible cementation. A hard lump of the cemented material collapses immediately when stood in a little water, but resets firmly on drying. A laboratory test by H. Birch, East African Agriculture and Forestry Research Organization,* shows that soluble salts can be precluded as a cause of this, and the cementation is attributable to the small clay fraction, coupled with a satisfactory distribution of particle sizes in the sand. The rapid softening on wetting means that rainfall penetration in the dunes is excellent. There can, however, be considerable run-off during heavy showers, when the lower areas between the dunes can become temporarily flooded with up to about 4 in. of water. In some areas the water tends to stand and in others it flows away. Such occasional washing would tend to wash the finer particles into the inter-dune areas and so reduce their permeability. Thus, on digging into the top of a dune, after a good shower of rain, the water penetration was found to be to about 2 ft.,

* A composite sample of samples 12 to 36 in. was taken, containing approximately 4·7 per cent. clay.

1. 20 g. of the sample were leached with 500 ml. of water, to remove soluble constituents. The residue dried out hard.
2. 20 g. samples were shaken with water and the bulk of the clay removed by decantation, giving two fractions, (*a*) clay, (*b*) sandy residue.

   (*a*) Clay: B.E.C. 78·5 m.e/100 g.

   (*b*) Sandy residue: this contained a small quantity of clay. Under these conditions the sample dried out hard, but when the clay was completely removed the samples dried out into easily broken aggregates.

   When the clay was mixed with the clay-free sands in the proportion approximately that in the original sample (i.e. 4 per cent. clay) and moistened, the resulting product dried out to a hard rock-like mass.

whereas in a depression about 15 ft. away and only 4 ft. lower the penetration was found to be only about 1 in. Occasionally, within the area of these low dunes, small pans may be found which are covered by a layer of small polygonal silty flakes (Plate IIIa). These are probably produced, in areas from which the rain water cannot drain away, by the same process carried one stage farther.

Good typical examples of these low chestnut dunes are to be found to the south-east of Lodwar before reaching Lorugumu. From about 12 miles beyond Lorugumu, although the country is still covered with similar sands, they tend to be somewhat redder in colour, and at Lorengipe, towards the escarpment, they become loamier and have a marked tendency to sheet erosion and the formation of dongas. The donga exposures locally show a tendency to columnar cracking. The somewhat redder sands in this region overlie a layer of old alluvial gravels. Their lowest horizon contains lime pellets which are also to be seen on the surface of nearby gravel exposures. In several of the more southern areas the dunes have reached an advanced stage in the process of removal by wind and rain. In many cases only a small hump remains to indicate the former dune and relief is now mainly flat.

The characteristic vegetation of these areas consists of widely spaced bushes of *Acacia misera* (Plate IIa). *Maerua oblongifolia* is often to be found climbing up in the Acacias. Loose blowing sand tends to collect around the base of the shrubs. In the coarse superficial sand between there are usually small and scattered brush-like plants, not normally exceeding 1 or 2 ft. in height. Of these *Sericocomopsis hildebrandtii* is the commonest. The blown-out sides of the dunes are bare, probably owing to the inability of seeds to secure a foothold on the hard surface. The absence of loose sand or suitable crevices means that there is nothing to stop them from being blown away before germination. As already seen, although these blown-out sands are very hard in the dry weather, they soften and absorb water during the rains, so their bareness is not likely to be due to moisture considerations. The lower-lying silty pans are also usually bare. In this case, however, there are ample crevices between the silty flakes to retain the seeds during the dry season and it seems likely that the virtual absence of vegetation may be due to lack of root water for the plants owing to the much poorer penetration observed in these situations.

The vegetation of the redder sands towards Lorengipe is generally denser than on the main plains. Well-spaced *Acacia misera* is still plentiful but there is an increasing admixture of other bushes, the low bush *Euphorbia spinescens* being particularly important. Near the escarpment *Sansevieria* and other succulents are also common. The differences, both of the soil and the vegetation, are in keeping with the somewhat increased altitude and higher-rainfall conditions associated with the proximity of the escarpment.

(*b*) *Rolling dune sands*

Immediately to the south of Lodwar there is a large area of dune sands of rolling relief; here the sand appears to be similar to that in the

low dunes farther to the west but is rather lighter in colour. The dunes are much larger and take the form of great dome-shaped undulations with crests up to several hundred yards apart. This area of rolling dunes extends to the east, towards Lake Rudolf, gradually flattening out and loosing its rolling relief until it resembles a sand sea. It was not examined in any detail but could possibly have originated as blown sand from the Rudolph basin. Generally speaking the whole surface is covered with loose sand, but within the dune area there are occasional large blown-out hollows which expose calcareous concretions. Beneath the sand there are also local exposures of waterworn gravels, which invite comparison with the lake terrace gravels north of the river (Section 2 (*b*)). One erosion hollow showed successive layers of wind-compacted sand changing abruptly at 2 to 3 ft. to a more calcareous horizon, which in turn overlay gravels (Plate IIIb). Others, near the Kamutili hills, showed very variable underlying gravels, including a locally consolidated conglomerate.

The vegetation over the whole of this area is distinct from that of the low-dune country to the west. *Acacia misera* is absent and the typical community is a wide spacing of *Balanites orbicularis* (a shrub lacking from the low-dune sands) in an almost pure ground growth of *Indigofera spinosa*. Other parts of this rolling dune area carry a low desert shrub community of *Euphorbia spinescens* and *Jatropha villosa*. This vegetation is akin to that of the lacustrine sands (Section 4 (*c*)).

(*c*) *Redeposited sands*

The sands included in this group are of practically the same character as those in the low-dune country. The principal differences lie in the absence of consolidated dune structure and in the evidence, observable in the field, of transport and redeposition by water action. The surface of the sand is commonly covered with a braided network of seasonal water runnels and the general relief is that of a flat sheet. Near areas of dune sands redeposited ones are often found occupying wide depressions at a slightly lower level, and in general it seems as though the main areas covered by this class originated as areas of dune sands or were at least close to them. The coarse deflated sand that forms ripples on the dunes is often to be found on top of the redeposited sands, but is here lighter in colour. Redeposited sands vary according to the distance that they have been transported from their parent dune areas; the farther they are away the more mixed they become. This category is designed to include relatively pure sands of this origin. If the sands are mixed with other soils in the area of redeposition they are placed with the flash-flood deposits (Section 3 (*a*)).

Large areas to the east of Lokichar and around Lorengipe appear to consist of redeposited sands. There are only very occasional low remnants of the old dunes and the whole area is flat with a slight tilt, which is quite enough for superficial water erosion to take place in heavy storms. Indeed a road, or what passes for it, may become partially obliterated or converted into a wide wash line. During transport and subsequent redeposition some sorting of the finer materials takes place. Such a sorting of the silt and the very small amount of clay accounts for the fact that,

in the lowermost areas of redeposited sands, standing water may sometimes be seen some days after the last shower. Examination of such sites shows that there is a local surface concentration of clay or silt, which prevents drainage, whereas the sand below is quite dry.

The typical vegetation of these areas contains some *Acacia misera* though this favours the low dune remnants. The vegetation on the purely redeposited sands is more mixed and variable, and patchy *A. misera* alternates with a low bush cover of *Euphorbia spinescens*. *Jatropha villosa* and *Asparagus* are also common. In some flat places in the vicinity of the major rivers redeposited sands carry spread clumps of the 'toothbrush tree', *Salvadora persica*. Superficial blowing of the sand here forms secondary hummock-like dunes around the clumps. These clumps are one of the most popular local sources of firewood and, after a period of settlement, they become cut out and any other vegetation very over-grazed. The hummock dunes are then blown away, leaving only flat and quite bare areas characterized by a litter of dead wood.

2. *Stone Mantles and Stone-mantle Soils*

The term 'stone-mantle soil' is here used to cover any truncated soil, soil remnant, or skeletal soil which has a layer of stones on the surface. In the main the formation is due to the well-known processes of desert erosion and deflation. The wash of periodic rainstorms and the desert wind remove the superficial soil horizons, thus lowering the surface and exposing any stones that may be in it, until there is a more or less continuous covering of wind-polished stones on the surface. Similar stony deserts are found in Libya, Egypt, and Algeria. Their frequency in Turkana is attributable to three main reasons. Firstly the erosion processes are liable to outstrip those of soil formation. Stony incipient or skeletal soils may thus be found which have been converted to stone-mantle formation under the present arid cycle, though they may scarcely have developed beyond the rotted-rock stage. Secondly there are extensive remnants of the land surface of an earlier, possibly Pliocene, cycle of erosion, which are found especially as extended pediments about the rocky hills of the basement complex, though also in lava areas. The main basement area of this type (running down the centre of the map to the south of Lodwar) is bounded by a low terrace bluff which is attributed by Dixey (1948) to subaerial erosion of the Pliocene surface (Plate IVb). These remnant land surfaces have been severely denuded and eroded down to or below the level of the lower stony horizons of their presumed former soil cover. Thirdly, waterworn stones and gravel are present in the Pleistocene alluvia and lake terraces, and these too lend themselves to stone-mantle formation by deflation. The result is a wide variety of types of stone covering ranging from bare stretches of massive angular rock litter to flats covered only with fine gravel. These 'soils' may be classified according to derivation as follows:

(*a*) Residual and pediment types.
  (i) Basement stone mantles;
  (ii) Lava stone mantles.
(*b*) Riverine alluvial and lake-terrace types.

In connexion with the residual stone-mantle soils mention should be made of a puzzling phenomenon. The hills of Turkana, to all appearance covered entirely by a litter of rock talus, show field evidence of a partial soil or rotted-rock horizon beneath the broken rock covering. This is to be seen especially in the local landslides among the lava hills, which regularly expose such an horizon. The presence of this substratum is also indicated by the emergence of tall buff-coloured termitaria from beneath the rock talus of both lava and basement hills. In certain instances, on the lavas, this may be due to an intercalated fossil-soil horizon. Elsewhere, perhaps, it may be postulated that the covering of rock litter, left by past erosion and deflation, may act as a protective covering, allowing the percolation of showers and at the same time checking further erosion and water loss after the fashion of a stone mulch. As a result of this a certain degree of protected weathering may still be proceeding in the layers beneath the unweathered stone covering.

(*a*) *Residual and pediment types*

(i) Basement-stone mantles. Stony litter 'soils' or soil residues of this class are most commonly identified by the presence of large amounts of angular or slightly rounded quartz rubble on the surface, together with outcrops of the basement complex. Quartz veins occur extensively in the basement rocks and the stones from them persist unaltered in the weathered material. Characteristically there are clean quartz stones on the surface with traces of soil between them. The surface traces are often orange-toned with rusty sand grains, but may pass beneath into a stony brownish or light-chocolate loam. Some of this remnant soil that is found between the stones in the pediment areas seems quite well developed and suggests that the stone mantle is the residue of the denudation of an ancient soil cover. Its existence below the stony surface is often indicated by the presence of termite mounds. There are also traces locally of a former covering of chestnut sands.

The more extensive pediment areas slope gently away from the foot of the hills with a well-graded surface which contrasts with the more irregular residual areas at the hill foot (Plate IVa). They probably represent the remnants of weathered material produced during the retreat of the scarp face, and as such must include material of colluvial origin. Planed-off outcrops of underlying rock are, however, also to be seen. The lower end of the incline often ends in a small bluff, 10 or 20 ft. high (Plate IVb), which then leads into flash-flood areas (Section 3 (*a*)). The lower areas towards the bluff are deeply gullied by streams which are now actively cutting back and producing an eroded relief of a 'badlands' type. By some of these watercourses deep beds of calcareous concretions are found; they are probably to be associated with former streamside alluvial deposits towards the lower end of the pediment slope.

The vegetation of these areas is characteristically variable, the species growing on the runnels differing from those growing in the intervening tracts. Very sparse *Balanites orbicularis* is the most typical species of the basement pediments and in some areas is practically the only shrub to

be seen; it is then commonly restricted to very shallow depressions and runnels (Plate IVa). Where there are chestnut-sand remnants there may be *Balanites* on the bare stone-mantle areas and *Acacia misera* on sandy patches. Where the basement stone mantles are regularly crossed by numerous small streams and runnels there is a regular alternation of vegetation types. Between the runnels there is very sparse *Balanites* with some *Acacia misera* whereas the runnels carry a thicker vegetation of *Acacia* and *Commiphora*. It is interesting to note that the basement hills and kopjes carry a much more developed community of small thorn trees, of which *Acacia senegal*, *A. mellifera*, *Boswellia elegans*, and *Commiphora* spp. are the commonest. It is also noteworthy that the vegetation on the basement hillsides is much thicker and richer in species than on lava hillsides.

(ii) Lava stone mantles. The lava stone mantles are found as fringes to lava-capped hill ranges and lava ridges, and in valleys intersecting them. In general the ground has a mantle of practically unweathered lava stones on the surface, often polished and fretted by wind action and with a characteristic 'patina' on their exposed faces. On the hills and ridges the stones are large, with occasional massive outcrops, but in flatter residual and pediment areas surrounding the hills they are much smaller and tail off to a small-chip mantle covering a deeper soil. The mantles appear to consist principally of the unweathered remnants of the harder and more resistant lava strata, though in certain areas they may include talus from the hills. In only one area, near Loperot, was the superficial stone cover found to be weathered to the extent that it would readily crack.

The presence of soil or partially formed soil under the more massive lava stone mantles of the hills has already been commented on. Landslides often reveal quite a deep exposure of pale pinkish rotted lava, and pale buff-coloured termitaria elsewhere indicate the presence of soil below the stone mantle. In the flatter sites the typical soil found under a lava stone mantle is a somewhat blocky-structured chocolate loam, plastic when wet, with soft calcareous concretions or small lime flecks in the soil (Plate VIa). The texture, however, varies to clay loam of a similarly calcareous character. This grades downwards into pinkish or pale purplish rotted lava where the soil is of a residual type. Pediment remnants also include areas of colluvial origin, which generally carry a smallish stone cover. The tendency to calcareous concretions is more pronounced than on the basement rocks and there is a more definite soil profile.

A large lava stone mantle pediment some 3 to 5 miles wide is to be found extending to the west and north-west from the north end of the Kamutili hills. The area to the south-east of Loperot consists largely of lava stone mantle soils, but there are also interbedded sediments which affect the soil pattern. Towards Kangetet there are dunes of soft sand lying on top of the stone-mantle soils. These dunes, unlike others in Turkana, do not seem to be remnants of an ancient and more extensive former dune area, and give the impression that they are in process of formation from sands brought in by the dominant easterly winds. The

lava belts lie to windward of the chestnut-sand zones and there are only very occasional traces of a former sand mantle.

Although lava stone mantles often show quite a depth of soil under the stones, vegetation on them is strikingly sparser and poorer in species than on the basement areas. Large tracts appear almost entirely bare, but there is generally an extremely widely spaced distribution of *Acacia misera*, practically confined to small runnels; the areas between have a very thin growth of *Aristida hirtiglumis*. The marked poverty of vegetation may possibly be due to poor water relations in the more clayey calcareous soil. Astonishingly enough these areas seemed frequently to be used by the Turkana for grazing sheep.

(*b*) *Riverine alluvial and lake-terrace types*

Wide shelves of very mixed alluvium, which were deposited in an earlier period, probably Pleistocene, are well exemplified along the river at Lorugumu and at several points within the next 8 miles to the south. These gravel banks consist of stones which have just had their sharp edges rounded and are of very mixed origin, the commonest being quartz and lava together with fragments of basement rocks. An admixture of fine-grained alluvium is found beneath the surface stone cover. The high degree of mixing points to past transport by very powerful river spates, which seem to have been responsible for extensive beds of this nature. Finer gravels are exposed near watercourses about Lorengipe and elsewhere to the south. Exposures indicate that these beds were subsequently largely overlaid by the chestnut sands. Where they are extensively uncovered, as near Lorogumu, many of the superficial stones show a marked desert polish together with a distinct pitting and fretting of the surface, and it is reasonable to assume that a great deal of deflation of the original beds has taken place. In the southern examples, as near Lorengipe, the gravelly alluvia, as well as the lower horizons of the chestnut-sand remnants that overlie them, show horizons of lime pellets. In some cases, near the larger watercourses, these pellets are perhaps to be associated with the old alluvium but in other cases it appeared more likely that they were residues of the basal horizon of the overlying sands or that they had formed in the underlying gravels through a process of downward leaching from this horizon.

Stone-mantle soils of the lake-terrace class are to be seen to the east and north of Lodwar. These belts lie parallel to and on either side of the hills, about 18 miles from Lodwar on the road to Lake Rudolf, and carry a covering of well-rounded quartz shingle. The stones are washed clean on the surface but locally show rusty iron staining below where there are gritty remnants of a truncated soil between the stones. Elsewhere in this area, about 9 miles east of Lodwar, there are old alluvial plains with a very thin layer of small water-worn gravel over a light-brown sandy loam, probably calcareous, which becomes loamier and lime-flecked below (Plate VIb). There is a little gravel throughout and the stone mantle has been produced by deflation of the finer materials. These areas are represented by Fuchs (1939) and Dixey (1948) as Pleistocene lake beds associated with the former higher level of Lake

Rudolf. In the case of the belt east of the hills flanking Lake Rudolf the gravel beds are found associated with large banks entirely composed of fossilized fresh-water oysters, *Etheria elliptica* Lam., each shell being rolled in a consolidated mixture of mud and grit.

In general the vegetation of these alluvial and lacustrine stone mantles is extremely sparse. A little scattered *Balanites* is found on the mixed alluvial gravels near Lorogumu, with some clumps of *Salvadora persica* near the river. The lacustrine shingle beds to the north-east of Lodwar have a few very widely scattered and rather small *Acacia misera*, together with a little brush-like vegetation on the runnels, but the gravel plains nearer Lodwar are completely bare.

3. *Flash-flood and Colluvial Sands*

Owing to the extreme sparseness of desert vegetation, the extent of stony hills and stone-mantle soils, sun-baked soil surfaces and the heavy though infrequent character of rain storms, run-off is locally severe and can take the form of a sudden sweeping surface wash which is referred to here as a flash flood. Such severe washing is most marked in its effect on hill slopes and stony pediments, and below the latter especially great expanses of rain-washed sand are deposited. These flash-flood deposits are characterized by their very mixed and variable make-up and by the belts of braided watercourses and runnels which cross them and shift their position from year to year. To them should be added a few local and restricted areas in the less extreme region in the south which represent a more normal colluvial accumulation from surrounding hills.

(*a*) *Flash-flood deposits*

The most highly developed flash-flood area seen lies below the small bluff that bounds the basement stone-mantle area west of the Lodwar–Lokichar road (Section 2 (*a*)). This stone-mantle tract still carries a few small remnants and caps of chestnut sand. During the rains part of these sand remnants together with other soil from the stone mantle is washed off wholesale on to the deposition plain below. The redeposited soils vary from yard to yard and it is clear that different showers must vary in the distance that they are able to carry the material. This variable sandy sheet is traversed by numerous quite wide shallow watercourses and many hundreds of smaller ephemeral channels which flow out of as well as into each other. The sand mixture varies through anything from a pale ochreous brown to a darker reddish chestnut in colouring and from a loamy sand to pure sand in texture. Greyer sandy soil, coming nearer to a true alluvium, is found by major watercourses and a pale fawn fine sandy calcareous soil occurs at lower levels. Owing to surface deflation, however, the whole mixture is masked by a thin superficial layer of coarse whitened sand. At the lower end of the deposition area there are small superficial accumulations of loose sand about 6 to 8 in. deep and up to 30 yards wide. These also are probably the products of deflation, and the ultimate result of the process is the formation of very shallow dune-like structures that are now in the process of growing (Plate VIIa). There are also a few areas that carry a very fine chip stone

mantle. Towards the south there are, indeed, areas between the main watercourses of almost bare stone-mantle soils. These areas may be partly flash-flood in origin but are probably mainly reduced remnant tongues which have been left as a lower surface following the retreat of the main pediment stone-mantle area.

The vegetation of the flash-flood areas is naturally patchy, but shows a marked contrast between watercourses and intervening areas. Tall vegetation is restricted to the main watercourses, which carry lines of *Acacia tortilis* on their banks, and in some areas they are so close together that the country appears to be covered with *A. tortilis* woodland. The force with which the flood waters come down these streams is sufficient to uproot trees and the wash lines are commonly littered with dead wood. In the areas between vegetation is either lacking or very much sparser, consisting in the main of very widely scattered *Acacia misera* and *Euphorbia spinescens*. The shallow patches of wind-accumulated sands carry small brush-like plants, of which *Indigofera spinosa* is the commonest.

(*b*) *Colluvial basement sands*

These are sands of mixed grain which have been directly derived from the basement soils of surrounding hills as a result of less drastic erosion processes and lack the braided pattern of the flash-flood areas. They occur typically as hillfoot aprons or as quite wide open areas surrounded by hills, where the hill wash has infilled a valley bottom. A few basement outcrops, together with their stone-mantle soils, emerge locally in the larger infilled areas. Kangetet is in one such small area and a larger one lies to the west, but they are otherwise of no importance.

The vegetation here is relatively plentiful and well assorted, no doubt owing to better rainfall near the hills. Thin and patchy *Acacia tortilis* woodland even occurs, while the more central areas have sparse *Acacia nubica* and *A. misera* together with occasional *Salvadora persica* over a better ground cover with some grass. Cattle are grazed where water is available.

4. *Alluvial and Lacustrine Soils*

With the last exception, the soils hitherto described are essentially the products of desert erosion processes. There remain true alluvial soils, formed by the flooding of the main rivers, and comparable deposits on the former floor of Lake Rudolf, which require to be briefly noted. These may be divided into (*a*) normal riverine alluvium, (*b*) calcareous silty plains found towards Lake Rudolf, (*c*) belts of lacustrine sands left by the retreat of the lake, and (*d*) small localized patches of very highly gypseous alluvium.

(*a*) *Sandy riverine alluvium*

As in other parts of Africa the most characteristic colour of recent alluvium is a light slightly greyish brown. The texture varies from a silty sand with a coarser sand admixture to a very powdery finer grained soil. Different intensities of river flooding carry the various materials

different distances and the deposits are normally banded. The lower parts of the profile show lime flecks or a lime nodule horizon, though this is not invariably present. Riverine alluvium, on any scale, is chiefly found along the banks of the Turkwell and its main tributaries, with narrower strips adjoining the minor streams. Locally, near Lodwar, these deposits widen into a small alluvial plain extending to the foot of the hills and carrying some hill debris.

The vegetation of riverine alluvium is markedly more luxuriant, ranging from a narrow line of *Acacia tortilis* and other trees along the small rivers to quite dense riverine forest of tall *Acacia* spp. and *Hyphaene* palms. Such dense forest is only found along the banks of the largest rivers, the Turkwell and the Kerio. *Salvadora persica* alternates with *A. tortilis* in some areas and *A. nubica* is characteristic of the sand-covered fringes of alluvial belts. Sorghum is occasionally grown in the bed of the Turkwell.

Two southern streams, the Geukumyuk and Korinyang, fan out into flat areas and, instead of having a single well-defined watercourse, flow through many small runnels spread over an area up to a mile wide. These areas are covered with a layer of alluvium and are occasionally used for growing sorghum. Their natural vegetation is a tall swamp grass, *Echinochloa pyramidalis*, over 6 ft. high. Areas that have been neglected after cultivation are rapidly invaded by *Acacia nubica*.

(*b*) *Calcareous silty plains*

In the area to the south-east of the Lodwar–Lake Rudolf road there are several square miles of silty plains. The typical soil here has a chalky pale brown colour and consists of a silty fine sand with a considerable clay fraction. These soils are highly calcareous and effervesce freely with acid. The surface is level and covered with small silty flakes. The whole area is quite flat, devoid of any well-developed drainage system and is flooded by standing water during the rains. The Turkwell delta is now about 5 miles to the east of it and the river a mile or so to the south. Today there are also mud flats to the south of the delta and it is likely that this soil represents an ancient deltaic mud flat associated with a somewhat higher lake level. The vegetation of this area is a remarkable uniform stand of *Acacia tortilis* with open patches.

A few miles from Lodwar to the west of the Lokitaung road there is a similar flat plain of silty fawn-brown calcareous soil carrying spaced *Balanites orbicularis*. Another area of similar pale fawn-brown, but somewhat more clayey, soils was found about 15 miles south-east of Lodwar in the lowest area between the N'gamatak and Kamutili hills. These appear to be highly calcareous fine sandy to silty clays, with the more clayey soils deeply split into cracks up to an inch wide. The vegetation on the cracking soils is grassland of *Lintonia nutans* and *Dinebra* sp. (Plate VIIb), but the less cracked areas are largely bare.

(*c*) *Lacustrine sands*

A broad belt of deep loose-surfaced sands lies to the east of the Lodwar–Lake Rudolf road (Plate VIIIa). These sands, of a light-brown

colouring, are shown to be of lacustrine origin by the presence of numerous small shells, and a roadside cutting showed several feet of shell-bearing fine packed sand. The shells tend to be more plentiful in surface patches than lower down the profile owing to surface deflation (Plate VIIIb). In general the relief of the lake sands is flat or slightly undulating. They have not been examined in any detail but it is probable that they were deposited in a comparatively recent regression of Lake Rudolf.* Blowing dune sands are still to be seen in the vicinity of Ferguson Gulf.

Spaced *Euphorbia spinescens* and *Balanites orbicularis* are plentiful on the rises of the sand belt and several species of low brush-like plants and small bushes of *Jatropha villosa* are general. Near Ferguson Gulf a large belt of wind-blown lake sands carries extensive stands of *Hyphaene* palms, about which secondary dunes are in process of formation.

(*d*) *Gypseous alluvium*

Certain small alluvial deposits were found lying alongside the west edge of the Kamutili hills which were of an olive-toned fawn colour and consisted of a silty fine sand mixed with small quartz fragments and coarse grit. There were sheets of fibrous gypsum exposed through the alluvium. Analysis showed that this alluvium contained 4,400 p.p.m. soluble SO_4. The area was quite bare and devoid of any vegetation. It may be noted that a dissected lava pediment a little farther to the north had gypsum exposed in flat sheets.

5. *Black- and Brown-Clay Soils*

(*a*) *Brown-clay pans*

This category refers to a rather chocolate-brown, fine sandy clay which effervesces freely with acid. It is deeply cracked, has a cloddy to crumbly structure and contains a few hard blackish calcareous concretions. One large pan, 5 miles across, containing such a soil lies about 8 miles to the south-east of Lodwar. The floor of the pan is quite flat and lies about 40 ft. below the level of the surrounding rolling dune sands (*vide* Section 1 (*b*)). The vegetation on the floor of the pan was very short grass of *Drake-Brockmania somalensis*, a grass usually associated with saline conditions.

* The following species of mollusca were collected and have been identified mainly by B. Verdcourt of the East African Agriculture and Forestry Research Organization.

Caelatura aegyptiaca (Caill.)
C. monceti (Bgt.)
C. rothschildi (Neuv. et Ant.)
Corbicula africana (Krauss).
Bellamya costulata (V.Mts.) var. *triliratus* (V.Mts.)
Cleopatra bulimoides (Oliv.)
C. pirothi Jick.
Melanoides tuberculata (Müller)

All these species, with the single exception of *Caelatura rothschildi*, the position of which is uncertain, are known to be living today, thus indicating that these lacustrine sands are relatively recent deposits.

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Country west of the Turkwell from 19,500 ft.

Right: Chestnut sand sheet with dune remnants undergoing incipient dissection

Left: Denuded and heavily dissected stone mantle area

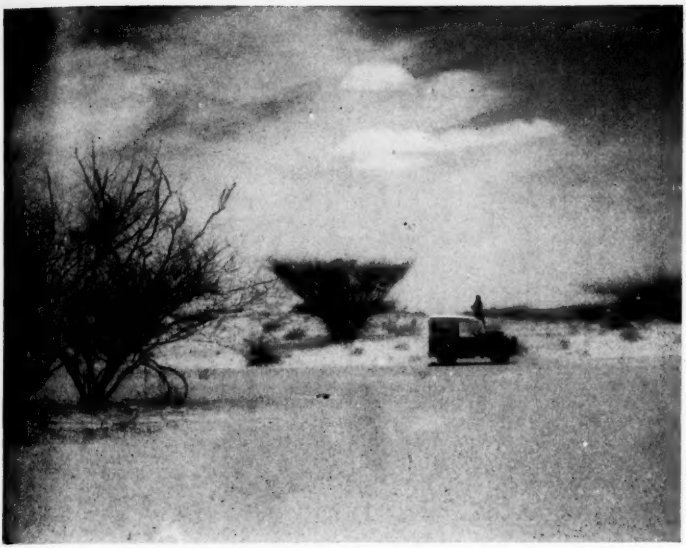
C. F. HEMMING *and* C. G. TRAPNELL—PLATE I

(*a*) Consolidated chestnut sand dune

Left centre: surface sand blown off, exposing the underlying cemented sand. Wind-fretted edges of compacted sand above the blow-out (see below for detail). Coarse rippled surface sand in foreground. Top capped with loose sand carrying *Acacia misera* and sparse ground vegetation

(*b*) Close-up of the wind-eroded crest of a small chestnut dune showing the fretted edges of numerous successive layers of compacted sand

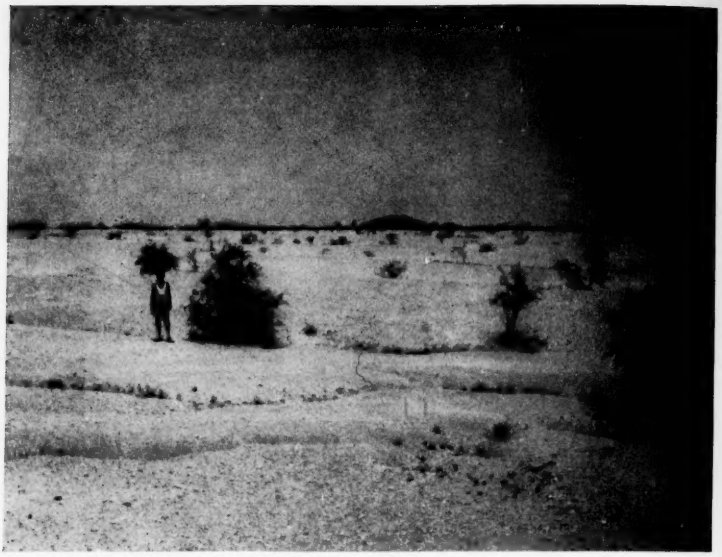
C. F. HEMMING *and* C. G. TRAPNELL—PLATE II



(*a*) Silty pan in the area of consolidated chestnut dune sands. Scattered *Acacia misera* with desert brush on loose sand on dune tops and pan margin. Note the absence of vegetation in the pan

(*b*) An erosion hollow in rolling dune sands, exposing underlying calcareous horizon and large area of water-worn gravel or shingle

C. F. HEMMING *and* C. G. TRAPNELL—PLATE III



(*a*) General view of basement stone mantle soils to the south-west of Lodwar. *Balanites orbicularis* and sparse ground vegetation in the runnels

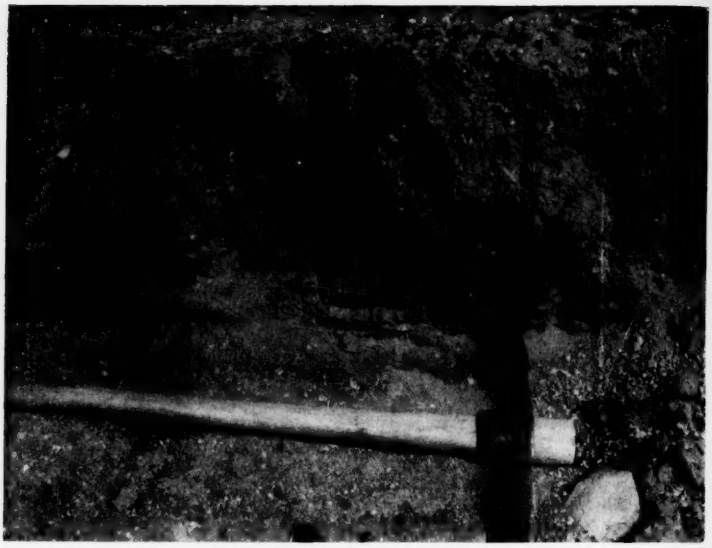
(*b*) The low bluff which divides the basement stone mantle soils above from the flash-flood areas below

C. F. HEMMING *and* C. G. TRAPNELL—PLATE IV

(*a*) Massive lava stone mantle area. Surface layer of unweathered lava blocks, weathered below. Very sparse vegetation on soil between boulders

(*b*) Small lava 'talus' stone mantle over lime-flecked light chocolate sandy loam. Sandy element may come from a former overlying sand mantle. Sparse *Acacia misera*

C. F. HEMMING *and* C. G. TRAPNELL—PLATE V



(*a*) Profile of a lava stone mantle soil showing a small chip type of stony surface over light chocolate-brown lime-flecked loam

(*b*) Alluvial or lake terrace stone mantle east of Lodwar. Water-worn gravel over light brown fine sandy loam, lime-flecked and loamier below

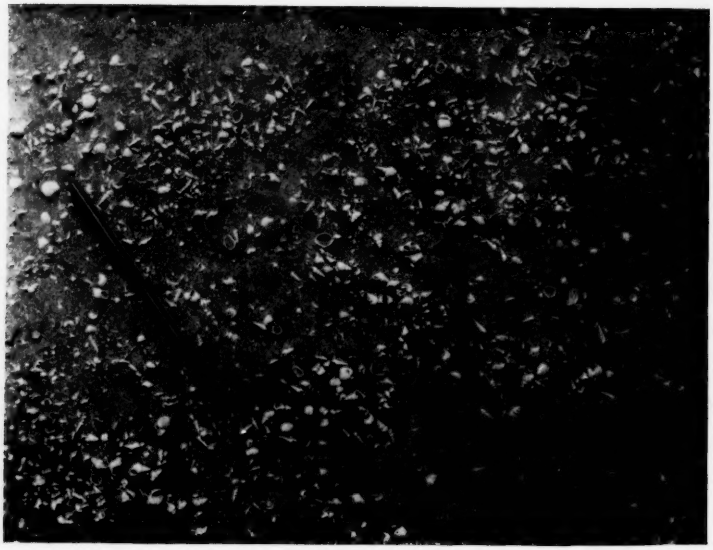
C. F. HEMMING *and* C. G. TRAPNELL—PLATE VI

(*a*) General view of lower flash-flood area. Bare patches of consolidated mixed sand with coarse surface sand. Low dune-like accumulations of soft wind-sorted sand with small brush-like vegetation. Thinly scattered *Acacia misera* and *Euphorbia spinescens*

(*b*) Seasonally moist calcareous clay area with good grass growth of *Lintonia nutans* on cracking soil. *Acacia misera* line behind

C. F. HEMMING *and* C. G. TRAPNELL—PLATE VII

(*a*) A wide expanse of lacustrine sands. Mainly consolidated, but some superficial accumulation of wind-blown sand around the bushes of *Euphorbia spinescens*



(*b*) Lacustrine sands: close-up showing the masses of shells exposed by deflation

C. F. HEMMING *and* C. G. TRAPNELL—PLATE VIII

(*b*) *Black-clay plains*

There are one or two very local occurrences of black-clay soils, which may have survived from earlier and less arid conditions. The principal occurrences lie along the western margins of the lavas extending northwards from Loperot, where crumbly black-clay plains with lime concretions were noted. Occurrences of travertine limestone were found in the vicinity (*vide* Fuchs, Appendix A, 1939). Towards the south-east of the flash-flood area near here there are traces of a blackish crumbly clay loam, with many soft calcareous concretions, underlying the flash-flood deposits. These underlying soils were detected owing to the presence of *Balanites orbicularis* growing in an area where the typical vegetation is *Acacia misera* (*vide* Section 3 (*a*)).

Adjoining the area of lacustrine sands there is also an area of small pans containing remnants of a blackish clay with many hard puppet-shaped blackish calcareous concretions. These seem to be blown-out areas of a similar soil which has been buried by lacustrine sands.

Supplementary Note

Further areas of the sands described here may be looked for in the dunes of the Chalbi and Koroli deserts east of Lake Rudolf, and extensive stony lava areas are indicated on maps of this region. Traces of superficial sand deposits and stones with aeolian faceting are occasionally also observable in less arid parts of Kenya, and may possibly reflect past conditions comparable to the Turkana régime. A review of the inferred sequence of development of the Turkana soil pattern will be found in the summary at the beginning of the paper.

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TURKISH FOREST SOILS

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Summary

An account of the distribution and botanical composition of Turkish forests is given along with analyses of some typical soil profiles. Extreme variations in climate have a strong influence on the country, and over large areas the low rainfall is a limiting factor for plant growth. The position is aggravated by soil erosion which has followed clearance of woodland. The results of mineralogical analyses of the clay fractions are discussed with reference to soil type, parent material, cation-exchange capacity, drainage and productivity of the soils.

GEOGRAPHICALLY Turkey consists in a simplified form of a narrow coastal plain from which rise steep mountain ranges encircling a large central plateau of semi-arid steppe country. Climatic conditions vary considerably with latitude and altitude giving great differences both in rainfall and temperature. The rainfall distribution curves (Fig. 1) drawn

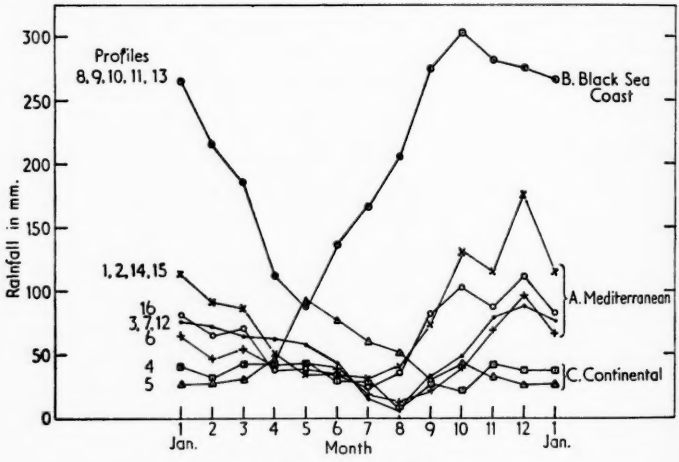

FIG. 1. Rainfall distribution.

from monthly data from several meteorological stations show three distinct climatic types. These are: *A* minimum precipitation in late summer and maximum in winter (Mediterranean type), *B* abundant throughout the year with minimum in early summer (Black Sea coast type), and *C* maximum in late spring and very low total (Continental type). The climatic regions are outlined on the map (Fig. 2).

FIG. 2. Map of Turkey showing forested area (shaded), sampling sites (circled), and climate regions.
A Mediterranean; B Black Sea; C Continental.

The geological formations in Turkey cover a wide variety of lithological types including sedimentary, metamorphic, and both acid and basic igneous rocks, and this, as well as the climatic variation, is reflected in the soils. In the absence of any Pleistocene or other recent glaciation there is very little contamination of the soil parent materials by erratic additions from neighbouring geological formations and, with the exception of alluvial deposits, the soils can all be considered as sedentary on the weathering rocks. The study of the processes of pedogenesis is therefore not complicated by the presence of mixed parent materials which so often obscures the picture in Britain and other northern European countries, where most of the soils are derived from transported glacial deposits of mixed origin.

The forest area of Turkey which totals about 10·5 m. hectares, or about 13 per cent. of the whole country, is mainly confined to the coastal mountain ranges and some isolated mountainous areas within the central arid zone which rise above the surrounding steppe country and consequently have a higher precipitation and can carry a forest vegetation (Fig. 2).

Coniferous and deciduous forests each cover about half the total wooded area, the former being of greater economic value. The total number of indigenous species is very large. Hardwoods predominate up to moderate elevations, and conifers on the higher mountain slopes. In the north the level at which the conifers become predominant is about 800 to 1,000 metres and the upper limit of the forests about 1,800 to 2,000 metres. The corresponding levels are somewhat higher in the south. In general the deciduous stands are on brown forest soils and the conifers on more leached podzolic soils.

In the Black Sea coastal region *Fagus orientalis* is the dominant species with *Quercus*, *Carpinus*, *Castanea*, and *Abies bornmülleriana*. *Pinus silvestris* and *P. nigra* cover the higher mountain slopes. *Picea orientalis* and *Abies nordmanniana* occur in the east, and *Populus*, *Tilia*, and *Fraxinus* are common in the west. In the Marmara region in north-west Turkey hardwoods prevail, *Quercus*, *Fagus*, *Ulmus*, and *Fraxinus* being prevalent. Conifers predominate in the Aegean Sea region; *Pinus silvestris*, *P. nigra*, *P. brutia*, and *P. pinea* are all found. *Quercus aeglops* and *liquidamber* are economically valuable and *Fagus* and *Castanea* are also present. Conifers also outnumber deciduous trees in the Mediterranean Sea region where *Pinus nigra*, *P. brutia*, *Abies*, *Cedrus*, *Juniperus*, and *Quercus* occur. In Eastern Anatolia adjoining Russia the conifers *Pinus*, *Picea*, and *Abies* dominate in the north but are almost completely replaced by the *Quercus* in the south. *Populus* and *Betula* also occur. In Central Anatolia in the centre of Turkey the density of wooded land is much less than in the coastal zones; hardwoods and conifers are equally represented, *Quercus*, *Pinus*, and *Juniperus* being the commonest genera.

On most of the coastal plains and lower mountain valleys and in parts of the central plateau agriculture is practised. Wheat, barley, maize, rice, millet, sunflower, cotton, vegetables, legumes, and fruit are the chief crops, and the livestock includes sheep, goats, and cattle. This

industry, which accounts for about 80 per cent. of the population, is dependent for its water-supply on the mountain ranges which receive a high rainfall, especially those facing the humid sea winds. The presence of forest vegetation on these mountains plays a vital role in regulating the water-supply to the lower-lying agricultural areas. The growth of the peasant population in recent years has necessitated an extension of the agricultural areas up the mountain slopes. Uncontrolled burning and clearing of the natural forest cover has resulted in soil erosion on a large scale, and the increase in grazing has seriously affected the natural regeneration of the forests. A reafforestation programme for these areas is essential; and one of the major economic problems facing Turkey today is to find a suitable and stable balance between agriculture and sylviculture which can absorb the rapidly increasing population (Heske, 1952).

The high relief has an important bearing on the forest soils (Irmak, 1952). Natural erosion keeps profile development at a young stage and there is usually a close relationship between parent material and such soil properties as colour and texture. The influence of greater leaching in the elevated areas is seen in the fact that most of the forest soils are pedalfers as opposed to the pedocals in the lower-lying agricultural areas.

TABLE I

Turkish Forest Soils

Profile No.	*Parent rock*	*Soil group*	*Elev. in m.*	*Temp. in °C.*	*Climatic group*	*Drainage*	*Quality as forest soil*
1	Diabase	Brown Earth	100	12·9	A	Good	Good (agric.)
2	Limestone	Terra Rossa	100	12·9	A	Good	Good
3	Diabase	Brown Earth	1,100	9·4	A	Good to 70 cm.	Good
4	Basalt	Brown Earth	1,100	9·3	C	Good	Moderate
5	Limestone	Chernozem	1,750	3·7	C	Good	Good (agric.)
6	Limestone	Rendzina	100	13·7	A	Good to 100 cm.	Moderate (agric.)
7	Limestone	Terra Rossa	730	11·4	A	Good	Good
8	Dolerite	Brown Earth Pod.	600	11·3	B	Fair	Moderate (agric.)
9	Dolerite	Brown Earth	300	13·3	B	Good	Moderate
10	Diorite	Brown Earth	1,650	6·3	B	Good	Good
11	Granodiorite	Brown Earth	900	10·3	B	Good	Moderate (agric.)
12	Biotite Gneiss	Brown Earth	1,500	7·4	A	Good	Good
13	Granite	Brown Earth	400	12·8	B	Good	Good
14	Shale	Brown Earth	100	12·9	A	Good to 70 cm.	Good
15	Sandstone and Shale	Brown Earth Pod.	100	12·9	A	Fair	Moderate
16	Granite	Brown Earth	100	13·7	A	Good	Good

The soils which have been recognized in the forest areas include: brown earths, podzols, podzolized soils with reddish B horizons, terra rossas, and rendzinas. Chernozems and chestnut earths occur in the eastern highlands. Associated soils with gley horizons also occur locally.

The nature of the organic surface layers under the forests varies considerably (Irmak, 1952). There is usually a surface litter, a well developed F layer and little or no H layer; sometimes F and H are both well developed. Occasionally there is only a litter with neither F nor H layers present; this is found in humid areas of the coastal zone below the 600 m. level where long warm wet autumns and mild winters favour the

prolonged activity of micro-organisms in the soil. In general, soils at higher elevations are richer in humus, but only rarely, as in the case of some brown earths under deciduous trees, is the colour effect of the organic matter visible below 20 cm.

One of the primary objectives of this investigation was to study the relationship between clay mineralogy and soil type. As no previous

TABLE 2

Mechanical Composition and pH *Values*

Profile No.		*Depth in cm.*	pH	*Coarse sand* 2·0–0·2 *mm.*	*Fine sand* 0·2–0·02	*Silt* 0·02–0·002	*Clay* (< 0·002)
				%	%	%	%
1	a	10–15	7·06	24·0	27·0	26·0	23·0
	b	20–25	7·10	26·0	24·0	23·0	27·0
2	a	10–20	6·88	6·0	23·0	17·0	54·0
	b	90–100	8·20	8·0	28·0	16·0	48·0
3	a	10–15	5·90	12·0	25·0	20·0	43·0
	b	70–80	5·98	2·0	35·0	28·0	35·0
4		10–20	6·48	21·0	35·0	25·0	19·0
5	a	20–25	7·69	14·0	22·0	24·0	40·0
	b	60–80	8·25	16·0	25·0	22·0	37·0
6		20–40	8·38	9·0	13·0	22·0	56·0
7		30–40	7·85	16·0	21·0	22·0	41·0
8	a	5–10	4·81	17·0	18·0	31·0	34·0
	b	10–20	3·75	15·0	22·0	26·0	37·0
	c	40–50	4·73	22·0	20·0	25·0	33·0
	d	100–110	4·70	23·0	22·0	24·0	31·0
9	a	5–10	4·93	29·0	35·0	23·0	13·0
	b	10–20	4·80	26·0	33·0	29·0	12·0
10	a	5–10	4·98	45·0	25·0	11·0	19·0
	b	20–30	4·88	43·0	26·0	11·0	20·0
11	a	5–10	4·80	25·0	35·0	20·0	20·0
	b	10–20	4·67	27·0	29·0	22·0	22·0
	c	40–50	4·62	21·0	20·0	24·0	35·0
	d	80–90	4·54	17·0	24·0	28·0	31·0
12	a	10–15	6·34	41·0	34·0	13·0	12·0
	b	50–60	6·15	36·0	35·0	14·0	15·0
13	a	5–10	5·60	..	..	..	..
	b	20–30	5·33				
14	a	5–15	5·97	15·0	44·0	21·0	20·0
	b	20–30	6·05	14·0	43·0	22·0	21·0
15	a	5–10	5·42	37·0	32·0	12·0	19·0
	b	70–80	5·46	38·0	30·0	10·0	22·0
16	a	5–10	6·66	48·0	30·0	12·0	10·0
	b	40–50	5·70	50·0	28·0	11·0	11·0

information on this subject for Turkish soils was available at the outset, it was decided to take a general view covering a number of different soils, and in most cases only two layers from each profile were sampled. This was justified by the results which showed that differences between the layers were usually small compared with differences between the profiles.

Characteristic data for the sixteen profiles sampled are given in Table 1,

and the mechanical composition, pH and depth of the samples are given in Table 2. The sampling areas are indicated on the map (Fig. 2) along with the numbers of the profiles from each locality.

The separation of clay for analysis was carried out by standard sedimentation methods. The percentage of clay below 1·2μ is given in Table 3 along with the percentage of the total ($<2\mu$) which is in this range. The figures show that in all cases the 0–1·2μ fraction makes up over 50 per cent. of the total clay, and in most cases over 70 per cent. In the four soils on limestone over 80 per cent. of the clay falls in the finer fraction. The 0–1·2μ fraction was used for the cation-exchange capacity determinations and for mineralogical analyses. A microdistillation method (Mackenzie, 1951) was used for the former. The X-ray techniques included diffraction by powder and oriented aggregate specimens (Mitchell, 1953), with pretreatments by glycerol saturation and heating to various temperatures. CoKα radiation and 9 cm. precision powder cameras were used. Treatment with boiling hydrogen peroxide was necessary to destroy organic matter in some of the surface samples, but this was avoided where possible. In a few cases hydrosulphite treatment (Mitchell and Mackenzie, 1953) was used to remove free iron and aluminium compounds to facilitate the identification of the clay minerals. The marked improvement in the diffraction pattern of some of the clays indicates the presence of amorphous iron and/or aluminium compounds.

Rough quantitative estimations were made from the powder diagrams either visually or by using a recording microphotometer for line-density measurements on films obtained from powder specimens containing an added internal standard (Mitchell, 1956). These methods are subject to considerable errors from a variety of sources and the figures given should be regarded as only approximations. Direct quantitative estimation of mixed-layer minerals is almost impossible in mixtures, and the values quoted were calculated by difference after estimation of the other components. The material identified as illite varied considerably, the first-order basal reflection was often broad and diffuse, and it is probable that the figures quoted for this mineral may often include some mixed-layer material.

The cation-exchange capacities of the 1·2μ clay fractions are given in Table 3 along with the mineralogical analyses. The profiles in this table, and in the preceding ones, have been arranged in decreasing order of the cation-exchange capacity of the lowest layer sampled. The values found for the surface layers were usually higher due to the organic-matter contribution. This arrangement brings the clays with a high montmorillonite content to the top, as would be expected, but the position of the high vermiculite clays seems rather puzzling as this mineral in the pure state usually has an exchange capacity at least as high as montmorillonite. The distinction between vermiculite and chlorite, however, is sometimes very difficult in soil clays when the diffraction diagrams contain much central scattering, and the former mineral may have been overestimated at the expense of the latter. The position in the tables of the clays with large amounts of mixed-layer minerals is

TABLE 3

Turkish Soil Clays arranged in Order of C.E.C.

Profile No.	*C.E.C. of clay* ($< 1{\cdot}2\ \mu$)	*% Clay* $< 1{\cdot}2\ \mu$	*% Clay* $\frac{< 1{\cdot}2\ \mu \times 100}{< 2\ \mu}$	*Kaol.** %	*Illite* %	*Verm.* %	*Mont.* %	*Chlorite* %	*M–L†* %	*Quartz* %	*Iron Oxides‡* %
1	113	21	78	5	45	..	50	..	..	..	..
2	109	40	83	..	..	..	95	..	..	..	5H
3	108	28	80	10	..	..	..	5	75 (*a*)	10	..
4	105	13	68	5	..	..	90	..	..	..	5L
5	94	35	95	10	60	..	30	..	..	..	..
6	81	51	91	10	..	..	25	..	60 (*a*)	5	..
7	66	35	85	25	55	..	..	10	..	5	5H
8	58	21	68	35 (H)	30	25	..	..	..	10	..
9	57	6	50	40 (H)	25	25	..	..	..	..	5H+5G
10	54	15	75	10	25	65	..	..	..	..	..
11	53	28	90	15	10	..	..	20	40 (*b*)	15	..
12	51	11	73	10	30	50	..	..	..	10	..
13	47	2·4	..	10	15	30	..	20	20 (*b*)	5	..
14	45	12	57	15	25	..	..	5	45 (*c*)	10	..
15	42	19	86	25	25	35	..	..	..	15	..
16	34	8	73	75 (K)	15	..	..	..	..	5	5L

* H = Halloysite
K = Kaolinite

† M–L = Mixed-Layer Minerals
(*a*) Montmorillonite-Illite
(*b*) Vermiculite-Illite
(*c*) Vermiculite-Chlorite

‡ H = Haematite
L = Lepidocrocite
G = Goethite

interesting. It shows that their cation-exchange capacity can vary over fairly wide limits. The mineral in profile 3 for example is a random interstratification of montmorillonite and illite units, and the capacity is obviously very high, while in profile 14 we have a mineral with a regular interstratification of chlorite and vermiculite layers, and the capacity, as would be expected, is much lower. On the whole the cation-exchange capacities are higher than those usually found for Scottish soil clays, and higher than would be expected from the generally accepted values for pure clay minerals, with the exception of those containing much vermiculite. The discrepancies may be due in part to underestimation of the amounts of mixed-layer minerals and to the presence of some organic matter.

It will also be noted that the arrangement in the table brings the parent rocks approximately into order of increasing acidity (in the geologist's sense). It has been found for Scottish soils (Mitchell, 1955) that the acidity of the parent rock is of importance in determining the mineralogy of the clay fraction, and it is interesting to find that the same correlation exists under such extreme climatic variations as occur in Turkey.

The content of kaolin minerals shows a wider variation than is found in Scottish soils, where it usually lies between 15 and 35 per cent. When the kaolin content of a soil clay exceeds about 25–30 per cent. it is often possible to identify the mineral species present; thus in profiles 8 and 9 on dolerite, halloysite was identified, and in profile 16 on granite, kaolinite was found. This is in agreement with the correlation found between acidity of the parent rock and crystallinity of the kaolin minerals for Scottish soils (Mitchell, 1955).

An interesting clay was obtained from the basaltic soil profile 4. This is almost entirely composed of montmorillonite minerals with only a trace of kaolin and lepidocrocite. The X-ray diagrams show two distinct (06) lines at 1·495 and 1·528 Å with the intensity ratio about 3:5 indicating a mixture of dioctahedral and trioctahedral montmorillonite minerals in about these proportions.

Four of the soils examined are derived from calcareous parent materials and they show great differences in their clay mineralogy. Of the two terra rossas, both formed under the Mediterranean type of climate, one on chalk (profile 2) has a highly montmorillonitic clay while the other (profile 7) on a hard crystalline limestone has illite and kaolin as its chief clay minerals. A rendzina formed on a recent calcareous clay (profile 6) under similar climatic conditions has a randomly interstratified illite-montmorillonite mineral as the main component of the clay. A chernozem (profile 5) also on calcareous clay from the area of continental climate is mostly illitic, but contains some montmorillonite.

The remainder of the soils sampled have all been classified as brown earths, although some of them show signs of podzolization, and should perhaps be classified as grey-brown podzolic soils. They occur under all three climatic conditions, but the variations in their clay mineralogy cannot be correlated with this.

The influence of drainage conditions on clay mineralogy is not noticeable. It will be seen, however, that all three profiles with a well-drained

surface and gleyed lower layers (i.e. 3, 6, and 14) contain large amounts of mixed-layer minerals, but this cannot be taken as significant in view of the small number of samples examined.

Any correlation that may exist between clay mineralogy and the quality of the soils for forestry (or agriculture) is completely masked by the huge variations in climate, and in the type of trees (or crops) grown. Taking the country as a whole the limiting factor for natural productivity of most of the soils is the low rainfall, and this will probably always be true in the case of the forest soils. Extensive use of irrigation on some of the agricultural land, however, is an economic possibility, and under such conditions soil differences may be reflected more strongly in productivity, and soil mineralogy may become an important factor.

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FEATURES OF SOME SEMI-ARID SOILS IN THE DISTRICT OF KHARTOUM, SUDAN

I. THE HIGH-LEVEL DARK CLAYS

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WITH FOUR PLATES

Summary

The topographic, climatic, geological, and vegetational setting of Khartoum is briefly described. The field characteristics of the main soil group, the High Level Dark Clays, are given, and the secondary minerals, the curved structures, and the interpenetrating horizons are described in some detail and their origins discussed. It is suggested that some features may be fossil.

Laboratory analyses show that the distribution of moisture, soluble salts, and sodium in the profile is uniform, with maxima in the second or third foot. Values in the top 6 in. are always low. The salts consist mainly of sulphate and chloride in the subsoil and of bicarbonate near the surface. The soil is strongly alkaline and consistently very low in organic nitrogen in all horizons.

The coarsest fractions of the soil consist chiefly of secondary minerals with some quartz, but as the fractions become finer, quartz grains become increasingly abundant. The chemical and mineral composition of the calcareous concretions is given, and they are shown to have formed by replacement. The habit and crystallography of the fibrous and lens gypsum is described and its mode of formation discussed. Microscopic examination of the minerals of the fine fraction showed that, as the content of the light minerals consisted almost entirely of quartz and that the percentage of heavy minerals in the total fine sand averages only 4·3 per cent., considerable weathering of the primary minerals must have occurred. From the species and proportions of the heavy minerals present, it is suggested that much of the material may have come from Sudan sources, and that colluviation may have played a large part in its formation.

The classification of the soil is discussed, and the name 'Solonized Sub-tropical Black Earth' proposed.

The Setting

KHARTOUM lies in the northern Sudan at the junction of the Blue Nile and White Nile (Plate I). To the south lies the Gezira, the clay plain on which most of the Sudan's long staple cotton is grown, and on the soils of which considerable research, summarized by Jewitt (1955), has been conducted. To the east lie the clay lands of the Butana desert and to the west the red sands ('Goz') of Western Sudan. Northwards, the soils become skeletal as the Sahara proper is reached. The land is one of extreme flatness; in the neighbourhood of Khartoum the variations in level are within 6 metres, not including the floodlands which, in the case of the Blue Nile, account for another 6 metres. Farther afield, the horizontality of the landscape is also striking, being broken only occasionally by isolated rocky hills.

The climate is dry and very hot for most of the year. The mean annual rainfall is 6½ in., and the temperatures have a mean maximum of 107° F. for May, and a mean minimum of 59° F. for January. The relative

humidity figures, even in the so-called rainy season, are low and reflect the general aridity of the climate, which becomes extreme in May and June. The powerful winds at this time raise dust storms ('habubs') which shift a good deal of fine material and cause considerable discomfort to the inhabitants.

The solid geology consists almost entirely of Nubian Series, which, however, is mostly buried under drifts. It appears at the surface at several places and consists of ironstone and sandstone which rest on finer-grained sediments of mudstones of various colours—white, red, purple. The Nubian Series passes eastwards under alluvium and other drifts, and from the evidence of wells and boreholes it is probable that these rocks underlie the whole of this district.

The vegetational cover is generally sparse or absent, and restricted to short annual grasses, chiefly *Aristida* spp. and *Schoenfeldtia* sp., with scattered scrub trees, mostly species of acacia. The grasses live for about two months, during which time the land becomes green, and then for the rest of the year they remain standing as brown dry 'hay' which is eaten off by goats and other animals to a degree which increases as the urban perimeter is reached. In the immediate vicinity of the towns the ravages of the numerous goats keep the ground almost bare.

The soils (Fig. 1) have been mapped chiefly on their topographical expression and on features shown in aerial photographs of the district. They divide clearly into three groups, of which the first, the High Level Dark Clays, is described in this paper.

The High Level Dark Clays

The area which extends from Khartoum southwards between the two rivers and south-eastwards into the Butana desert consists of the High Level Dark Clays. They lie on flat land a few metres above the high level of the rivers, from which they are separated by a band of varying width of alluvial soils.

They show a remarkable uniformity in their profiles, which consist of three horizons: the top a sandy-textured brown/red-brown soil, followed by the main horizon of dark grey-brown clay, followed by a buff-brown horizon of varying texture (Fig. 2 and Plate II). There are many similarities to the Gezira soil as described by Greene (1928*a*), and the differences may be attributed in part to the more arid conditions of the Khartoum district. The features of special interest are the secondary minerals, the structures, and the relationships between the horizons.

The secondary minerals consist of concretions of calcium carbonate and crystalline aggregates of gypsum, but there are no iron or iron-manganese concretions as occur in the black soils of Ghana and Kenya. At the surface and in the first horizon occur small, hard, grey or black nodular concretions, while farther down the profile and well embedded in the soil are larger white or brownish-white concretions which increase in size downwards. The grey concretions are sometimes found deep in the soil, but these have evidently fallen in from the surface, and it appears probable that they form either at or very near the surface. Gypsum occurs mostly as fibrous crystals, but is also found as small

lenticular plates and sometimes as ill-defined aggregates. It is almost entirely confined to the second (clay) horizon and the fibrous gypsum concentrates at 2 to 3 ft. from the surface, and there too the crystals are the largest. The fibrous gypsum is reminiscent of geological 'beef' and occurs bridging gaps in the curved structures in the soil (Plate III), but not in the vertical cracks, a fact which is probably significant in the mode

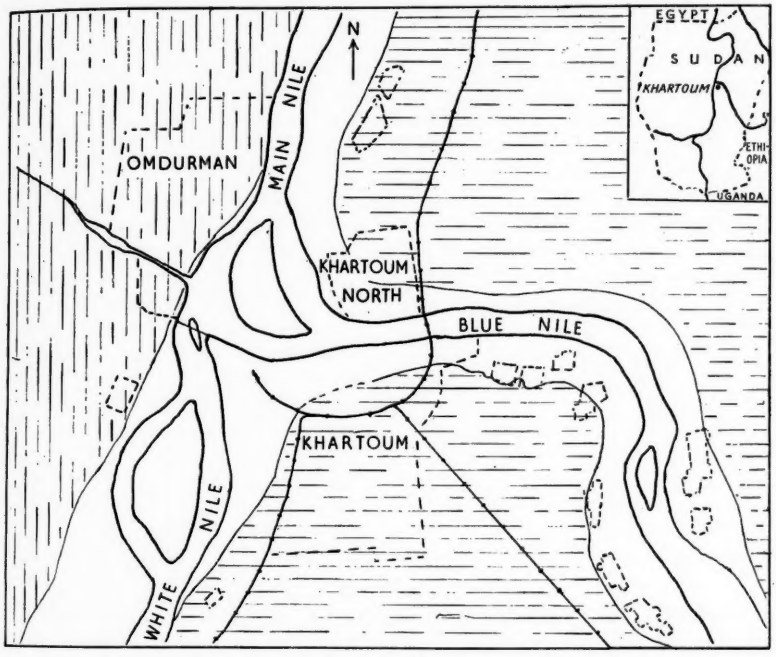

FIG 1. Map of the Khartoum District, showing boundaries of soil groups
(Scale: $2\frac{1}{4}$ miles = 1 in.)
Horizontal lines: High-level dark clays. Vertical lines: Red sand-ironstone soils.
Blank: Riverain soils.

of formation of this habit of gypsum. The crystals are about 1 cm. in length, though some have been found over 1 in. long. The lenticular gypsum occurs as very small plates, commonly less than $\frac{1}{2}$ cm. across, either singly or in aggregates, the lenticles showing no preferred orientation. Unlike the fibrous variety, this form occurs in the body of the soil, not in spaces, and at a higher level. The smallness of the lenses makes them easily overlooked, but they have been found much larger elsewhere in the Sudan.

The structures consist of large vertical cracks, more or less infilled with brown material from the surface, and curved oblique cracks which are not infilled. The vertical cracks are sharply picked out by the different colour and texture of the infill, and may extend to 5 ft. from the surface though the average is about half this. The surface of the cracks is rough

and irregular, in contrast to the oblique structures which are smooth and polished and sometimes grooved like slickensides in rocks (Plate IV). These oblique structures are curved and restricted almost completely to the second horizon in which they increase in size downwards. This

1
2
3
a. 1–2″ coarse sand, red-brown, structureless, dry.
b. 10–12″ loamy coarse sand, brown/grey-brown, prismatic, black concretions, penetration of H2, dry.
30–40″ sandy clay/clay, grey/brown-grey/black, oblique structures with slickensides increasing in size downwards, vertical cracks with infill of brown sand and concretions, fibrous gypsum most abundant at three feet, white calcareous concretions scattered throughout, slightly moist.
sandy clay/clayey sand, pale brown/yellow brown, compact, structureless, white/buff calcareous concretions concentrated near the top, dry.
• Black concretions
o White concretions
Curved structures with gypsum

FIG. 2. Diagram of profile of High Level Dark Clays

kind of structure has been reported from other parts of the world and described in detail by Krishna and Perumal (1949) in India, and it appears to be restricted to clay soils in monsoonal or sub-tropical countries. The writer has observed small structures of this kind in several parts of the Sudan, but in the Khartoum district they may be very large, in one instance over 10 ft. long. Such structures form slip surfaces over which the upper soil may slide, a fact of some importance in trench

digging in this district. They appear to be caused by differential movement of soil units resulting from swelling and contraction, but not through gravitational slip as described by Krishna and Perumal since these structures may occur on perfectly flat ground. The fact that they are best developed in the moistest part of the profiles and in clay with a high swelling coefficient favours the swelling–shrinking theory, but the presence of fibrous gypsum in gaps of up to 1 in. across suggests that if this was an annual movement it has long since stopped, that the soil has shrunk to a stable volume, thus allowing the gypsum crystals to form, possibly *pari passu* with the shrinking. There is certainly insufficient moisture at the present day being added to the soil during the rains to account for such large changes in volume, and the crystals of gypsum are too large to be dissolved and reform in so little water.

The horizons of the soil are of special interest on account of the sharpness and interpenetration of their boundaries. This and the differences in texture are such constant and striking features of the first and second layers that it seems probable that they are not true horizons but formerly two distinct transported materials laid down at different times. The field evidence suggests that the second (clay) layer was once at the surface, that it later dried out, cracked, and became covered with drifting dust and sand. The drifted material initially filled the cracks in the clay, giving the profile its interpenetrating appearance, but this process evidently occurred once and the feature is now a fossil one. Reasons for this view are based partly on the sharpness of the two layers—there appears to have been no real mixing of them as would be expected if the event were an annual one—and partly on the fact that at the present day insufficient moisture penetrates the soil to permit such extensive swelling and shrinking, and the cracking that does occur is limited to the top few inches. The fossil nature of the lower part of this soil is also indicated by the nature and amounts of gypsum, as has already been stated.

The change of colour from dark grey-brown in the second horizon to a pale brown colour in the third horizon is a regular occurrence which has been observed in other clay profiles in the Sudan and is noted in profile descriptions of black clay soils in other sub-tropical countries. In the Sudan the depth of this horizon appears to increase as the latitude decreases and it is probably related to the increase of rainfall which occurs from north to south. The difference in colour is not connected with the organic matter content as this is consistently low throughout the profile, but probably with the increased amount of calcium carbonate which often concentrates as buff concretionary masses near the top of the third horizon (Plate II).

Interpenetration of the second and third horizons may also occur, and detached masses of brown can be seen in the grey, and grey veins penetrate the brown. This is associated with a sharp change of texture, and it appears that in the north-east of this district this horizon was formerly a land surface which was later covered by muddy waters.

These soils have been analysed for a number of characteristics, and of these the soluble salts, sodium content, moisture, and minerals, including secondary minerals, have proved of most interest. The first

three of these are commonly determined in the dry soils of the Sudan as being indicative of their fertility, and in this district many soils have been so analysed. Their mean values have been expressed graphically (Fig. 3), and in all three characteristics the values for the second and third foot levels are highly significant at $P < 0{\cdot}001$ from the other levels

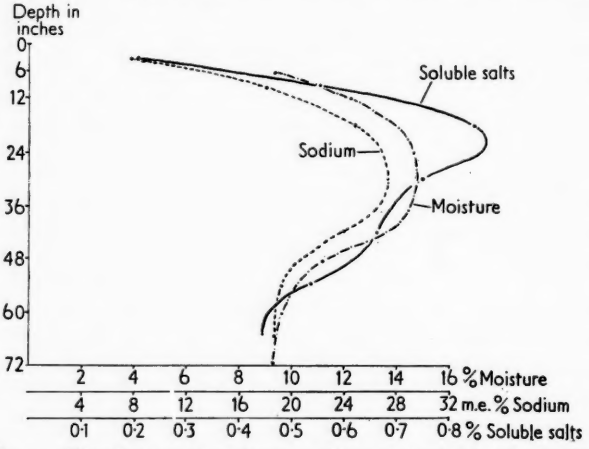

FIG. 3. Distribution of moisture, sodium and soluble salts in the profile of the High Level Dark Clays

in the soil. There is a regular and characteristic distribution curve of amounts in the profile, rising from low values rapidly to maxima in the second or third foot, followed by a more gradual decrease farther down the profile. These results are similar to the findings of Greene (1928, *a* and *b*) for Gezira soil, except that in the Khartoum district the point of maximum appears to be a little higher in the profile than is the case in the Gezira, a fact which is best explained by the lower rainfall of the Khartoum district. The amounts of soluble salts and sodium are of interest in being uniformly high, with a mean maximum of 0·84 per cent. at the 12–24 in. level for soluble salts, and of 27·1 m.e. per cent. at the 24–36 in. level for total sodium. These figures are much higher than those for other soil groups in this district, and although the top foot is always much lower in sodium and total soluble salts, the soils would be classified according to the Sudan system as rather bad to very bad agricultural land, and chiefly for this reason very little has been recommended for development. Pump schemes* on these soils have achieved variable results, sometimes fairly good, and some rain-grown *dura* (*Sorghum vulgare*) is sown every year, though the plants are stunted to about 2 ft. or less, and yields are very low.

Certain other properties are as would be expected. The soils are strongly alkaline, the pH in nearly all cases ranging between 8 and 9·5. There is little difference with depth, though there appears to be a slight decrease of alkalinity where the content of soluble salts is at its maximum.

* Areas of agricultural land irrigated by pump.

This was also found in Gezira soils, but the reason given there, that carbonate in the topsoil was responsible for the higher alkalinity, is not true of these soils. Of other radicals measured, nitrate is generally low, though it may concentrate in the salt horizon; available phosphate is low, and carbonate is generally absent. Organic nitrogen is very low in all horizons, the maximum recorded being 0·112 per cent. and the minimum 0·014 per cent.

An examination of the minerals of the soils was made by sieving out the coarse grades for inspection with a lens, and separating the fine sand into light and heavy fractions with bromoform for microscopic examination. The lens examination confirmed and extended the field observations in showing that the coarse fractions consist of a mixture of primary and secondary minerals, the primary consisting almost entirely of quartz, but including a little felspar, and a variable amount of brown mica, and the secondary minerals consisting of calcareous concretions and gypsum crystals. There are differences with depth and grade: differences in size and colour of the concretions with depth and the restricted occurrence of gypsum have already been mentioned but differences in the composition of the grades were also observed, secondary minerals being dominant in the coarse grades, and quartz in the finer grades. The black concretions have been analysed and are mainly calcium carbonate, but include some silica, iron, aluminium, and manganese, the last probably being responsible for the dark colour. Thin sections of both black and white concretions showed that they consist almost entirely of finely crystalline calcite, the mass being cracked and veined and often infilled with coarser-grained calcite. In the black concretions there is a rim of dark mineral consisting of dendritically arranged aggregates of black granules which 'grow' inwards, and also occur as patches in the body of the concretion. In the white concretions the dendrites occur only in the body of the concretion. From this, and the nature of the occurrence of the concretions in the soil, it is suggested that they all form initially as white concretions, but those at or near the surface develop a black patina due to the migration of manganese dioxide to the periphery, thus acquiring a 'desert glaze'. The occasional presence of heavy minerals including hornblende, brown mica, and zircon, shows that the concretions formed by replacement of soil not by displacement. The occurrence of quartz in the concretions is not very common, which suggests that it is less resistant to replacement by calcite than certain other minerals such as hornblende.

An examination of the lens gypsum showed that it consisted of aggregates or single lenses, each of an oval shape which is related to the crystallography of the mineral. Unexpectedly, the perfect (010) cleavage runs along the length of the mineral at right angles to the curved surfaces (Fig. 4). This is quite regular, and shows that these crystals have developed along their *b* axis at the expense of their *a* axis, contrary to the development of the selenite form of gypsum. No layering could be observed to account for the curved surfaces, which were rough and irregular as if they had formed by filling up lens-shaped gaps in the soil.

The degree of rounding of the coarse grades as well as of the fine sand

shows no uniformity, and all stages from angular to rounded may occur. Gastropod shells, usually fragmented, occur at all levels, and by a study of these from various parts of the Gezira, Tothill (1946) was able to show that moister conditions obtained when they lived than are experienced today.

In the fine sand the percentage of heavy minerals in the specimens

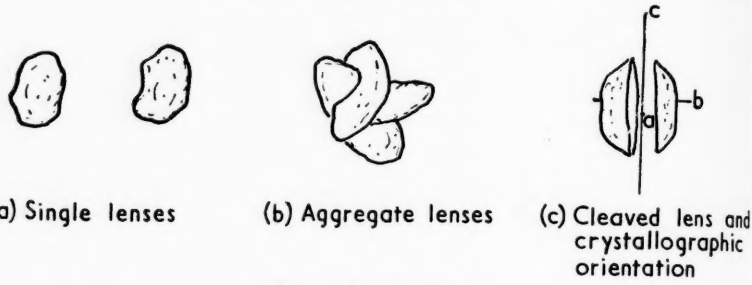

FIG. 4. Lens gypsum
(Enlarged about 3 times)

examined ranged from 1·4 to 8·8 (Table 1). Although these figures are higher than occur in most English sediments they are not very high if the materials were derived directly from primary rocks, and much weathering must have occurred before or after their emplacement. This view finds support in the analyses of the light fractions which consist almost entirely of quartz, and felspars are usually less than 1 per cent. As most igneous and metamorphic rocks contain more felspar than quartz, there must have been considerable weathering of these soils to have so reduced the percentage of felspar. Nearly all the grains are angular, suggesting that they were water-borne, not wind-borne, and that they were not transported great distances.

There is considerable uniformity in the amount and kinds of mineral from one place to another and also in the horizons, though it was anticipated that these would show differences due either to different weathering conditions or to different sources of parent material. The minerals identified were: quartz, chalcedony, orthoclase, microcline, plagioclase, hornblende, chlorite, augite, hypersthene, zircon, apatite, olivine (?), rutile, tourmaline, brown mica, garnet, sillimanite, monazite, epidote, zoisite, kyanite, staurolite, opaque minerals consisting of magnetite, ilmenite, leucoxene, limonite, and compound grains consisting usually of quartz and an opaque mineral. Of these, the commoner and more easily recognized heavy minerals have been counted. The opaque minerals, hornblende, and augite together form 85 to 90 per cent. of the total heavy minerals. All others are very subordinate, except for epidote which is always a prominent though not an abundant mineral in these soils. This mineral has been found in greater amounts in clays farther south in the Sudan, and is indicative of a metamorphic source of the soil. The abundance of hornblende is of interest as this is the dominant mineral in much of the metamorphic rock of the south and south-east

TABLE 1. *Approximate Percentages of Minerals in the Fine Sand Fractions of the High Level Dark Clays*

	Heavy minerals																Light minerals		
	Opaque	*Hornblende*	*Augite*	*Zircon*	*Apatite*	*Rutile Red*	*Rutile Yellow*	*Tourmaline*	*Mica*	*Garnet Red*	*Garnet Colourless*	*Sillimanite*	*Epidote*	*Kyanite*	*Staurolite*	*% HM. of total fine sand*	*Orthoclase*	*Plagioclase*	*Quartz*
RH 6 Horizon 1	25	35	25	:	∨ 1	:	:	:	:	3	:	∨ 1	4	∨ 1	∨ 1	5·8	3	1	96
,, ,, 2	20	42	18	3	:	2	:	:	∨ 1	:	:	∨ 1	3	:	:	4·0	2	∨ 1	97
,, ,, 3	40	30	10	4	:	:	1	:	:	2	:	∨	4	:	:	1·6	2	∨ 1	97
RH 9 Horizon 1	45	15	25	2	∨ 1	:	∨ 1	:	∨ 1	1	:	∨ 1	3	:	:	1·4	1	:	99
,, ,, 2	40	20	24	1	1	:	∨ 1	∨ 1	:	1	:	∨ 1	2	:	:	4·2			
,, ,, 3	30	38	16	2	∨ 1	∨ 1	∨ 1	:	:	2	:	:	5	:	1	2·7	6	∨ 1	93
RH 22 Horizon 1	40	25	8	2	1	∨ 1	1	:	∨ 1	2	:	∨ 1	10	:	:	1·5	1	:	99
,, ,, 2	44	32	7	∨ 1	:	1	∨ 1	:	:	2	1	:	4	:	:	4·5	5	1	94
,, ,, 3	58	18	12	1	∨ 1	∨ 1	∨ 1	:	:	1	:	:	3	:	:	5·2	2	∨ 1	97
RH 28 Horizon 1	40	32	16	2	:	:	1	∨ 1	1	1	:	1	3	:	∨ 1	3·0	∨ 1	∨ 1	98
,, ,, 2	42	30	20	1	:	∨ 1	∨ 1	:	1	∨ 1	:	∨ 1	1	:	:	2·8	∨ 1	∨ 1	98
,, ,, 3	48	15	35	∨ 1	:	:	1	1	1	:	:	∨ 1	1	:	:	8·8			
RH 58 Horizon 1	28	28	26	1	∨ 1	∨ 1	∨ 1	1	2	1	∨ 1	∨ 1	2	∨ 1	1	5·8	22	7	71
,, ,, 2	26	24	32	∨ 1	∨ 1	∨ 1	∨ 1	∨ 1	1	∨ 1	∨ 1	∨ 1	1	∨ 1	∨ 1	4·8	16	4	80
,, ,, 3	30	24	20	1	1	∨ 1	∨ 1	∨ 1	1	1	:	1	1	:	:	8·7	1	∨ 1	98

of the Sudan. The rarity of the metamorphic minerals kyanite and staurolite, on the other hand, is noteworthy, and also the virtual absence of that ubiquitous and variable mineral, tourmaline.

These analyses give some pointers to the origin of the soil. Because of the presence of purple augite it has been suggested by Andrew (1948) that the Gezira clay has been formed by sediments brought by the Blue Nile from the basaltic area of Abyssinia, but it does not seem likely that the High Level Dark Clays in the Khartoum district are entirely derived in this way because of the abundance of hornblende and the presence of epidote. Their presence in the clays farther afield, and in other soil groups in the Khartoum district, suggests that the parent material of these soils may have derived in part from more local sources, such as hornblende schist and calcareous schist. Other features of the soil, including the occasional presence of stones, and the absence of stratification, suggest that these clays were not laid down by normal sedimentation from river floods or extensive lakes, but by colluviation.

It is difficult to classify these High Level Dark Clays. They are undoubtedly related to the Gezira soils, which in turn have similarities to other clay soils in the Sudan. They bear some resemblance to the Sub-tropical Black Earths, in particular in being dark coloured, heavy textured, cracking, deep, alkaline, cloddy, and plastic, having a high base-exchange capacity, a low organic-matter content, a montmorillonite clay (in part), and containing abundant calcareous concretions. They differ in their high soluble-salts status, their gypsum, their high alkalinity, and, to some extent, their colour. In these features they more resemble solonetz and the saline-alkali soils described by Richards (1954) and others. But the rounded columnar and laminated structures and certain other features characteristic of solonetz do not occur in these soils, while on the other hand, the infall of the top horizon causing interpenetration and the curved structures with their fibrous gypsum are characteristic of these soils but not of solonetz. It is probable that these soils have 'pseudo-profiles', that is, they are built up of two, and in some cases three, layers of transported materials. The main clay horizon may be regarded as lying between the Sub-tropical Black Earths and the Saline-Alkali soils, and could best be described as 'Solonized Sub-tropical Black Earths'.

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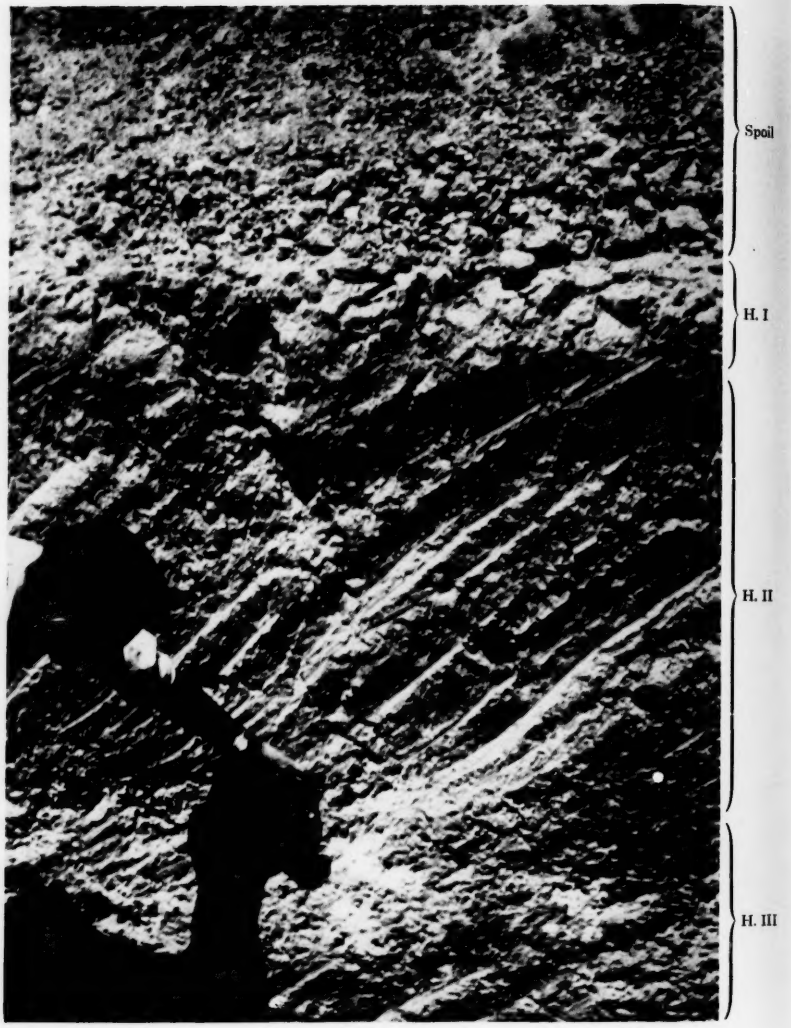
Aerial view of the Khartoum District, looking south

G. A. WORRALL.—PLATE I



Profile of High Level Dark Clay, showing three horizons and concretionary carbonate in Horizon III

G. A. WORRALL—PLATE II

Gypsum in cleavages and scattered calcareous concretions

G. A. WORRALL—PLATE III

Curved structure (below shilling) and sandy infill (top left)

G. A. WORRALL—PLATE IV

FEATURES OF SOME SEMI-ARID SOILS IN THE DISTRICT OF KHARTOUM, SUDAN

II. THE RED SAND-IRONSTONE GROUP AND THE RIVERAIN GROUP

G. A. WORRALL

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Summary

Two soil groups in the Khartoum district are described. The Red Sand-Ironstone Soils are characterized by a reddish sandy upper horizon, a second ironstone gravel horizon, and a third stony horizon, often consisting of kankar. They are dry soils, and contain very little soluble salts or plant nutrients, and the minerals are largely quartz and iron ores. The few heavy minerals show resemblance to those of the High Level Dark Clays in particular in their amounts of hornblende and epidote.

The resemblance of the red sand to the 'Goz' and the ironstone gravel to murram of laterite areas is noted and discussed, and evidence is produced for attributing the origin of both to the weathering of the rocks of the Nubian Series, and the soils are regarded as intrazonal.

The Riverain Soils of the Blue Nile and Main Nile have very variable textures, but the White Nile Clays are remarkably uniform in texture and profile. The differences can be attributed to the difference in the régime of the rivers. Salinity is also variable, but usually much lower than in the High Level Dark Clays, and the more saline soils are heavy-textured and lying in slight depressions.

The mineral content is similar in all the Riverain Soils except for the White Nile Clays which show some differences, and also similar to that in the High Level Dark Clays. The sources of the minerals are discussed, and a suggested mode of formation of the flood plain, by which islands link with the mainland, is proposed.

In a previous paper the main group of soils in the Khartoum district, the High Level Dark Clays, was described. Two other groups, the Red Sand-Ironstone Soils and the Riverain Soils, occupying the west of the district and the flood plains of the rivers respectively, remain to be considered.

The Red Sand-Ironstone Soils

West of the Main Nile and the White Nile and lying on rocks of the Nubian Series are red sandy soils containing ironstone gravel (Fig. 1). The land is nearly flat, but is dissected by *wadis* which deepen towards the river and often expose the underlying rock.

These soils have little in common with the High Level Dark Clays previously described. They consist fairly regularly of a reddish-brown loamy sand top horizon, followed sharply by a layer of small rounded dark brown ironstones, followed by a stony layer which may be either buff-coloured kankar or rock rubble from the Nubian Series.

A typical profile is as follows:

Horizon 1: 20 in. red-brown loamy sand with scattered pea-iron gravel; structureless; sharp to H. 2.

Horizon 2: 30 in. dark brown pea-iron gravel, fairly uniform size, averaging 5 mm., loosely bound by calcareous fine earth and containing scattered pieces of ironstone and sandstone; fairly sharp to H. 3.

Horizon 3: 10 in. buff stony layer of angular pieces of ironstone with some pea-iron and kankar, in a calcareous matrix.

In places the ironstone gravel may appear at the surface and continue down the profile without a loamy sand upper layer. This also occurs extensively to the east of Khartoum outside this district, and appears to

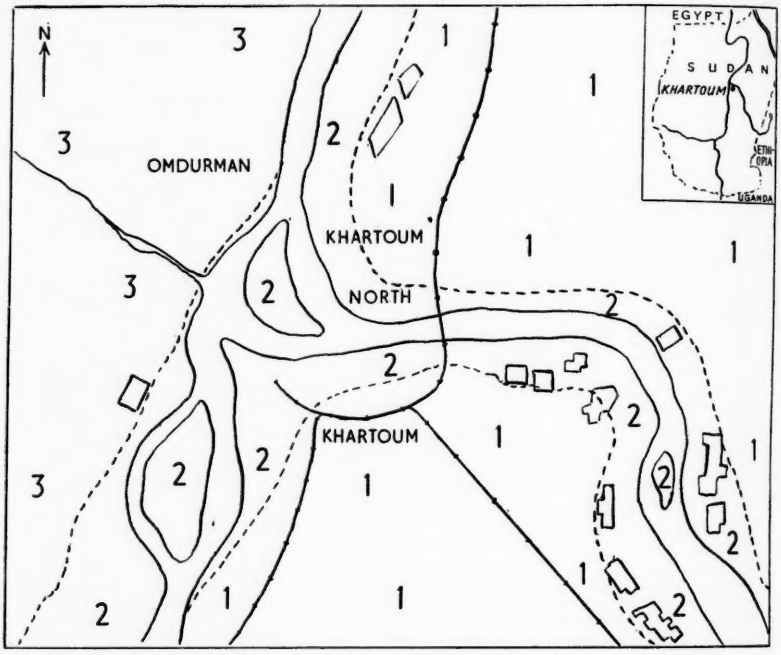

FIG. 1. Map of the Khartoum district, showing boundaries of soil groups.
1. High Level Dark Clays. 2. Riverain Soils. 3. Red Sand-Ironstone Soils.

be due to differences in deposition, and not to erosion. Also some red sands occur containing little or no ironstone gravel, and similar soils, extending over large areas of Western Sudan, have been described by Jewitt (1950).

The profile is of special interest both for its ironstone gravel and its kankar-like calcareous concretions. The latter occur low in the profile, forming a whitened zone, and differ from the concretions of the High Level Dark Clays in being larger, softer, and concentrated in one horizon. They are restricted to areas near the rivers, and do, in fact, resemble the tufa or river carbonate forming in the Nile today. The ironstone gravel consists of small dark brown stones of fairly uniform size, mostly ranging between 0·3 and 0·7 cm. in diameter, approximately rounded, and having a surface which is slightly nodular and glazed. They form the second horizon together with a matrix of fine earth and sand, and may also occur scattered in the sandy top horizon.

The chemical characteristics of these soils are also very different from the High Level Dark Clays. Both their soluble-salt status and sodium status (Fig. 2) are very low, and show very little variability in the profile. The content of soluble salts in the third foot averages 0·018 per cent.,

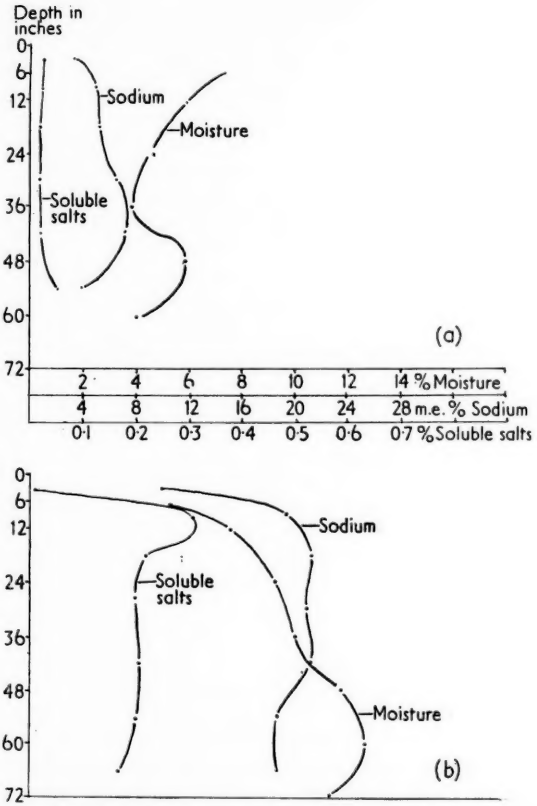

FIG. 2. Distribution of moisture, sodium, and soluble salts in Red Sand-Ironstone and Riverain Soils.
(a) Red Sand-Ironstone Soils. (b) Riverain Soils.

and of sodium 6·4 m.e. per cent., as compared with 0·84 per cent. and 27·1 per cent. respectively in the High Level Dark Clays. They are also very dry soils, and their poor retentivity for moisture probably accounts for their low values for soluble materials generally and also for their relatively low pH values which range from 7·5 to 8·4. However, as it is unlikely that these soils have ever been inundated by the Nile, and the Nubian Series have no saline beds, it may be that alkalinity and salinity have had little opportunity of developing. The same reason may account for the fact that there are extensive clay lands outside the Gezira which

have low values for soluble salts, and in some areas of the 'Goz' (red sands) the soil reaction may be slightly acid, though the climatic conditions favour salinity and alkalinity.

The high permeability may also be responsible for the well-weathered condition of the soils, though, as they are probably derived from Nubian Series rocks, it is likely that they were well weathered from the beginning. The light minerals (Table 1) consist of over 99 per cent. quartz, and the heavy minerals consist largely of opaque iron ores, and these appear to be mostly secondary. The small amount of primary minerals, however, shows a similarity in species to those in the High Level Dark Clays, notably in the amount of epidote.

The origin of these soils appears to be from the Nubian Series. The ironstone gravel in them has been examined by the geologists Grabham (1926) and Sandford (1935) who regarded it as a lateritic product formed in a hot humid climate, and Sandford connected it with the massive laterite-like rock he found in the north-west Sudan. Arkell (1949), however, by finding paleoliths *in situ* underlying the gravel, showed that at one point at least it was transported material. Although the writer has found fossil laterite similar to that described by Sandford at two places to the east and within 50 miles of Khartoum, it is localized in its occurrence, and does not appear to be directly connected with the gravel. In the Khartoum district there is much bedded ironstone in the Nubian Series and the gravel appears to be derived from it. In several pits a gradation from broken flat pieces of ironstone at the base to the rounded gravel higher in the profile was observed, and the gravel is restricted to areas where the Nubian Series is not far from the surface. Likewise, the red sand appears to be derived from the Nubian Series. The 'Goz' of the Western Sudan has been studied by Edmonds (1942) who decided it was derived by weathering and wind action from the Nubian Series farther north, and the writer's observations of red sand to the east of Khartoum have led him to a similar conclusion. It has frequently been observed that red sand occurs in the erosion channels in the hills of Nubian Series, and their bases are surrounded with it, and also where ironstone gravel occurs, bedded ironstone is frequently to be found in the hills in the vicinity. The derivation of the sand seems to be certain and the only further comment to be made is that the reddening process appears to be continuing at the present time, though Edmonds's view was that it occurred in a moister climate than obtains today. If this were so it would be expected that the sand would have all been blown or washed off the hills long ago. The course of weathering or erosion which has produced the ironstone gravel, however, is obscure. Its similarity to murram or, as the material is called in the Southern Sudan, pea-iron gravel, is very striking, and if its occurrence were more widespread in the Northern Sudan, a similar mode of formation might be postulated. It is evident, however, that it forms from fragments of bedded ironstone, there being some redistribution of iron to form the nodular pieces. Iron is not generally considered to be mobile in alkaline conditions, but it is a common observation that surface stones in deserts may take on a ferruginous glaze, and this has also been observed elsewhere in the Sudan.

TABLE 1

Approximate Percentages of Minerals in the Fine Fractions of the Riverain Soils and Red Sand-Ironstone Soils

TABLE I

Approximate Percentages of Minerals in the Fine Fractions of the Riverain Soils and Red Sand-Ironstone Soils

	Heavy minerals													Light minerals		
	Opaque	*Hornblende*	*Augite*	*Zircon*	*Apatite*	*Rutile Red*	*Rutile Yellow*	*Tourmaline*	*Mica*	*Garnet Red*	*Garnet Colourless*	*Sillimanite*	*Epidote*	*Kyanite*	*Staurolite*	% *HM. of total fine sand*	*Orthoclase*	*Plagioclase*	*Quartz*
Riverain Soils	(Blue Nile and Main Nile)																		
RH 7 Horizon 1	35	22	20	2	..	..	I	..	I	I	I	I	12	..	..	3·4	I	..	99
,, ,, 2	38	20	23	I	I	I	I	..	..	2	I	I	10	..	..	4·3	2	..	98
,, ,, 3	30	30	22	I	..	..	I	..	..	2	I	I	2	..	..	2·6	5	..	95
RH 17 Horizon 1	43	25	14	2	I	..	I	I	I	I	I	I	5	I	..	2·4	I	I	98
,, ,, 2	38	18	27	I	..	..	I	I	..	I	..	I	2	..	..	2·2	10	I	89
,, ,, 3	40	20	28	I	..	..	I	..	..	I	I	..	4	..	..	5·2	2	I	97
RH 19 Horizon 1	40	14	30	2	I	I	I	..	I	I	I	2	5	..	..	4·9	2	I	97
,, ,, 2	43	25	18	I	..	..	I	..	I	I	..	I	3	I	..	6·2	4	I	95
,, ,, 3	40	24	25	I	I	..	I	I	I	I	..	2	I	..	..	6·9	I	I	98
	(White Nile)																		
RH 38 Horizon 1	40	22	10	I	I	I	..	..	I	I	..	2	3	..	I	9·2	2	I	97
,, ,, 2	40	30	6	I	I	I	I	..	I	I	I	2	4	..	..	5·9	2	I	97
,, ,, 3	30	30	12	..	I	..	..	..	3	I	..	3	5	..	..	8·2	2	I	97
RH 40 Horizon 1	40	18	14	3	..	I	2	..	..	I	..	10	4	..	..	2·6	I	I	99
,, ,, 2	52	15	10	I	..	..	2	I	I	I	..	4	2	I	..	2·8	I	..	99
,, ,, 3	42	20	14	..	..	..	4	..	..	I	..	9	3	..	..	3·3	I	I	99
Red Sand-Ironstone Soils																			
RH 41 Horizon 1	70	8	4	6	..	I	I	I	..	I	I	I	4	..	I	1·7	I	I	99
,, ,, 2	68	6	4	8	..	I	I	I	..	..	I	I	5	..	I	1·8	I	I	99
,, ,, 3	60	15	3	8	I	I	2	I	..	I	I	2	5	..	I	3·3	I	..	99
RH 42 Horizon 1	60	10	3	7	..	I	4	I	..	..	..	..	3	..	..	3·3	..	..	100
,, ,, 2	75	5	I	9	..	..	2	I	..	..	..	I	4	..	I	7·7	I	I	99
,, ,, 3	72	2	..	11	..	2	2	2	..	..	I	..	4	I	..	12·7	I	I	99

Like the High Level Dark Clays, these soils do not fit readily into any classification. The red sands link with the 'Goz' of the Western Sudan, which in turn have been linked by van der Merwe (1955) with sands in Nigeria and the Kalahari, and the suggestion might be made that they are 'climatic' groups of soils. But their difference from other soils in the same climatic zone, as, for example, the clays adjoining the 'Goz' in Western Sudan, and the extension of the sands across climatic zones indicate, as van der Merwe (1955) has stated, that the parent materials have a dominant influence. The association of ironstone gravel with the sand, however, appears to be a unique soil form. Its nearest representatives are the murram soils of the Southern Sudan and East Africa, but these are acid soils and their texture loamy rather than sandy, and their origin is almost certainly different. They are best classified as Intrazonal soils, developed on a ferruginous facies of the Nubian Series.

The Riverain Soils

In the Northern Sudan the Nile system has a flood plain for much of its course, but it is usually less than a mile wide, and often consists only of 'gerf', that is, the sloping bank of the river which is exposed as the Nile flood subsides. In the Khartoum district it is well developed except on the west bank of the Main Nile where the Nubian Series rocks are exposed.

Like alluvial soils generally, these soils are very varied in texture, and anything from 90 per cent. sands to 70 per cent. clays may be found. The soils of the White Nile, however, are remarkably uniform, for they consist of a pale grey clay containing 60 to 70 per cent. clay. This heaviness and uniformity is due to the slowness and regularity of the White Nile and the fineness of its suspended matter. The soils of the Blue Nile and Main Nile are much more varied and have little in common except that, in heavy soils, the texture generally becomes lighter with depth, often changing sharply from clay to silt and later from silt to sand, and frequently having a carbonate horizon at the upper junction due to impedance of rising water and subsequent evaporation and precipitation. The amounts of soluble salts are almost as variable as the texture, and it is difficult to generalize, except to note that the amounts are almost always less than that in the High Level Dark Clays and that the maximum is commonly nearer the surface. There is some correlation with texture, in that light silty soils are always low in salt, the variation occurring in the clays. In these, the variation appears to be due to differences in microrelief, the low spots collecting the salt. The microrelief is more important than the salt content of the two rivers, as the White Nile, which has a higher content of sodium salts than the Blue Nile, has clay soils in this district with low values for soluble salts.

The coarse fractions of the Blue Nile and Main Nile soils resemble those of the High Level Dark Clays, and consist of black and white concretions and quartz, the last increasing in the finer fractions and the white concretions increasing down the profile. The White Nile Clays, on the other hand, have hardly any material above the Fine Sand grade, an indication of the slowness of the river and the fineness of its load.

Gypsum is rare in all the Riverain Soils. The heavy minerals (Table 1) closely resemble those in the High Level Dark Clays, the chief differences occurring in the amounts of hornblende, sillimanite, and rutile which are higher in the White Nile Clays, though not in the other Riverain Soils. In this connexion the work of Shukri (1950) on the minerals of the Nile sediments is of importance. He found distinct differences between the minerals of the Blue Nile and the White Nile, the first containing a dominantly igneous suite and the other a dominantly metamorphic suite of minerals, though in the vicinity of Khartoum he found that there was contamination of the sediments. The writer's work bears out Shukri's results in so far as there is more of the metamorphic suite in the White Nile Clays, but the minerals of the other Riverain Soils have also considerable amounts of metamorphic minerals, and the similarities in the varietal features do not favour the view that they are derived from widely different localities. It is suggested that these soils, like the High Level Dark Clays, have derived much of their material from relatively local sources. For example, the abundant hornblende could be derived from local granites or from the hornblende schists which have a widespread occurrence to the south-east of this district. Similarly, the amount of epidote is much greater than would be expected if the source of these soils was from the basalts of Abyssynia, whereas calcareous metamorphic rocks which might provide the epidote occur to the south-east. However, further discussion is unprofitable until more is known of the rocks over which the Nile system flows.

The mode of formation of the flood plain containing these soils is not certain. The common régime of rivers is to build up their beds and banks and from time to time to change their course to a lower level, but this does not appear to have occurred here, though it has been observed elsewhere in the Nile system. In this district the process appears to be one of shoal formation, the shoals later becoming islands, and still later linking at one end to the mainland. The closed channel, which can only receive slowly moving water, gradually silts up with fine deposits, and the river, because it is confined to the remaining open channel, becomes more erosive and the outer side of the island is attacked and material carried away to be added to other islands or to begin new ones. Islands in various stages of formation and linkage may be observed in this district (see Plate I of previous paper), and it is possible that the flood plain as a whole may have developed in this way. This mode of occurrence may also explain the elongated basins of the Northern Province of the Sudan. These are low-lying areas behind the river bank that can be flooded annually, and it seems probable that they are former channels of the Nile that have been cut off and are very slowly silting up.

Conclusions

The High Level Dark Clays described in a previous paper and the two groups described here are the main groups in the Khartoum district, and the great differences in their characteristics, including their colour, texture, structure, soluble salts, and pH, are very striking, as is the uniformity of characteristics within the groups, especially the High Level

Dark Clays and the Red Sand-Ironstone Soils. The explanation appears to be that the original differences in parent materials are still prominent, and that the interaction between these and past climatic events have left a greater impression than has the present climate. Thus, the most obvious characteristics of colour and texture are due to differences of parent material, while the amounts and distribution in the profile of the soluble salts and secondary minerals generally appear to be due to the interaction of climate, texture, and topography in a material already containing these ingredients or to which they were added by flood waters. Other features such as deep cracking and kankar formation are evidently the result of climatic conditions which were different from those obtaining today.

Acknowledgements

The writer would like to thank the Sudan Government Chemist, the Sudan Government Geologist, and the former Chief of the Research Division, Wad Medani (Dr. T. N. Jewitt), for permitting access to the files of their departments; P. E. T. Allen, Esq., of the Survey Department for providing aerial photographs; the Principal, Wye College, and Professor R. L. Wain for the use of library and laboratory facilities; Mahmoud Eff. Mahommed Siraj El Nour for his great help in carrying out some of the routine laboratory analyses; and Professor J. H. G. Lebon for his supervision of the work and encouraging interest in its progress.

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NITROGEN STUDIES ON THE IRRIGATED SOILS OF THE SUDAN GEZIRA

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Summary

The seasonal variation in the organic- and nitrate-nitrogen content of Gezira soil under irrigated rotational cropping has been studied over six successive years. Accent so far has been placed on the cotton phase of the rotations and statistical analysis of the results has shown that the organic-nitrogen content of the soil is not increased by rotational cropping beyond an equilibrium value which is presumably a function of the environmental conditions.

Increase of organic nitrogen in Gezira soil appears to be a function of seasonal conditions. Loss of organic nitrogen in marked excess of what could conceivably be explained by crop uptake is a definite feature. The loss occurs gradually throughout the whole season, giving a minimum organic-nitrogen content in the soil during the hot dry period of February to May.

Accumulation of nitrate-nitrogen, on the other hand, is dependent on the nature of the rotation and the period of the year. Nitrate accumulates at the beginning of the rainy season when it is rapidly leached to lower soil depths; it also accumulates on the bare fallows during the hot dry season. This latter finding is in accord with the statements of other workers.

THE social economy of the Sudan Gezira is much influenced by the large fluctuations in cotton yields that are such a marked feature of the crop when grown on Gezira soil. It is believed that these fluctuations are related to the nitrogen status of this soil. Much work has already been done on soil nitrates (Tothill, 1948; Jewitt, 1950) under various cultural treatments and different rotations. It was considered, however, that the total organic-nitrogen fraction required investigation. Since the mineralized nitrogen represents a variable and, in one case at least (Griffith, 1951), a potentially large fraction of the total soil nitrogen, it was very necessary also to follow, side by side with the organic fraction, changes in the mineralized fraction of which nitrate nitrogen is the only constituent of appreciable importance under Gezira conditions.

Research on these lines has been carried out at the Gezira Research Farm at Wad Medani over the period 1946/52. The lengthy period of the study and the very large number of samples involved, together with the low nitrogen content of Gezira soil, permitted a statistical appraisal of results. It was thus possible to differentiate between small real changes in nitrogen content and random variations in nitrogen content arising from the heterogeneity of the soil system.

Materials and Methods

The region known as the Gezira† is a featureless plain of which about

* This work was undertaken while the author was on the staff of the Research Division, Ministry of Agriculture, Wad Medani, A.-E. Sudan.

† For a description of the Gezira Scheme see Bluen (1931), Crowther and Crowther (1935), Gregory, Crowther and Lambert (1932), and Norris (1934), and for soil studies see Joseph (1925), Greene (1928, *a* and *b*), and Greene and Snow (1939).

one million acres are cultivated for cotton growing under irrigation. The climatic régime is arid—16 in. of rain annually, falling mainly in July and August—and the soil is a heavy intractable impermeable clay (60 per cent. less than 0·002 mm.) high in total salts and exchangeable sodium and low in carbon and nitrogen.

Field samples for the investigation were taken at regular intervals over extended periods from one long-term rotation experiment at the Gezira Research Farm, viz. the 'Three-Course Rotation' (see Crowther and Cochran, 1942). Five rotations are included in the 'Three-Course' experiment:

1. Cotton, fallow, fallow . . . CFF
2. Cotton, dura, fallow . . . CDF
3. Cotton, dura, dura . . . CDD
4. Cotton, lubia, fallow . . . CLF
5. Cotton, dura, lubia . . . CDL

Dura = *Sorghum vulgare*; Lubia = *Dolichos lablab*.

Rotations 1 and 4 approximate more closely than the remaining three to that practised in the main commercial cotton-growing area of the Gezira. Some aspects of the field management of these five rotations have an important bearing on certain conclusions drawn from the present study and must therefore be mentioned. Thus the fate of crop residues is important in comparing rotations whether from the point of view of yields or in terms of nutrient balance in the soil. In these experiments, after the removal of the seed cotton, the sticks are burnt outside the plots. The dura grain is removed, but the straw is eaten by penned sheep on the plots. The complete lubia crop is consumed on the plots by the folded sheep. In addition fallow weeds are not allowed to ripen, but are subjected to a system of fallow weeding. This has already been described by Crowther (1943) who discovered that the method gave rise to appreciable yield increases. Theoretically, all is thus eventually returned to the land except that contained in the cotton sticks and seed and the dura head.

Results are quoted for top-foot soil samples of the cotton phase of each rotation during successive seasons, except for 1948/9 when the three phases of rotation 1 (CFF) were sampled for analysis. Holes were dug in the eastern and western halves of each subplot and thorough field sampling was ensured by mixing *in situ*, on a plate, soil from the east and west face of each hole. Eight samples per sampling date per rotation were therefore analysed.

Organic nitrogen on samples from these rotations was determined on fine soil (passing 1-m. sieve) by the Kjeldahl method. 1 g. soil was used per determination, first being wetted with 2 c.c. distilled water and allowed to stand for 15 minutes before addition of 4 c.c. concentrated nitrogen-free sulphuric acid and 1 g. catalyst mixture ($Se : Na_2SO_4 = 1 : 9$). This pre-wetting technique is in accordance with Bal's modification (1925) of the Kjeldahl method, which was found by the writer to be applicable to the heavy Gezira clay soil. Furthermore, as pointed out by Madhok and Fazzal Uddin (1945), pre-wetting prevents partial

reduction of nitrate nitrogen and hence increased values for organic nitrogen. This was found to be effective in this respect with Gezira soil, so that nitrate nitrogen can be completely eliminated without affecting the organic nitrogen.

Time of digestion was standardized at 45 minutes since it was possible to obtain results thereby with 3 per cent. precision. The digestion mixture was then made alkaline with caustic soda and steam-distilled by the method of Pregl (1937), modified by using a considerably larger Kjeldahl distillation flask. Distillation was continued into N/100 hydrochloric acid until approximately 100 c.c. distillate were obtained, and the excess acid was titrated against N/100 caustic soda from a 5-c.c. burette (calibrated to 0·05 c.c.) using methyl-red indicator. During the course of the investigation all samples were analysed in duplicate and results are expressed in the text on an oven-dry basis. Nitrates were determined separately by the phenol-disulphonic acid method.

Results of Chemical and Statistical Analyses

The cropping season for cotton in the Gezira is considered as beginning in May when the land is cleaned and cultivated in preparation for sowing in August. The season ends in April following the pulling-up and burning of all cotton debris. Seasons subsequently quoted, as for example 1946/7, involve the period May 1946 to April 1947. Results of the soil organic-nitrogen analyses over the seasons 1946/7 to 1951/2 are presented in Tables 1–4. Analyses of variance were carried out for the organic-nitrogen and nitrate-nitrogen figures in order to establish whether observed changes in the nitrogen content were significant (the $P = 0{\cdot}05$ level was used in all cases and significant differences which are quoted were all calculated at this level).

With the exception of seasons 1947/8 and 1948/9, organic-nitrogen figures are presented as means for all five rotations on each sampling date since there was no statistically significant interaction between rotations and dates. In 1947/8 there was a significant interaction and results for each rotation separately are therefore presented (Table 3). In 1948/9 variability of nitrogen values around the mean value was found to be significantly different between phases. It was found to be greatest in the first fallow phase and least in the cotton phase. This is plausible since the first fallow phase would have most root residues in the soil and these might cause greater variability. There was a significant interaction between sampling dates and phases; results for each phase are given in Table 4.

Analyses of variance for the nitrate-nitrogen figures showed that in all seasons there was a significant interaction between rotation and sampling date. Complete presentation of the data would be lengthy, but results averaged over all rotations are shown in Fig. 1 which serves to emphasize main trends. It will be appreciated, however, that differences established statistically are thereby obscured due to the rotation-date interaction. Results for season 1948/9 are quoted separately in Table 5 in view of certain features which are embodied in the later discussion.

TABLE 1

Organic-nitrogen Values in p.p.m. as Means for the Cotton Phase of all Five Rotations*

Seasons	*1946/7*	*1947/8*	*1948/9*	*1949/50*	*1950/1*	*1951/2*
Sampling dates in months		See Table III.	See Table IV.			
March	..			..	..	..
April	..			..	..	..
May	239			299	184	185
June	257			281	229	281
July (i)	275					
(ii)	274			278	239	284
(iii)	304					
August (i)	295			279	237	288
(ii)					242	
Sept. (i)	298			270	244	289
(ii)					240	
Oct.	..			271	234	284
Nov.	..			267	237	286
Dec.	..			*268*	*240*	*287*
Jan.	..			269	237	276
Feb. (i)	..			265	235	276
(ii)	..			264		
March (i)	..			265	233	273
(ii)	..			258	234	
April (i)	..			264	230	274
(ii)	..			245		
May	357			211	235	..
Sig. diff.	9·1'			9·6	9·8	4·2

* Parts per million of soil.

TABLE 2

Organic-nitrogen Values in p.p.m. as Rotational Means over Whole Season

Seasons	*1946/7*	*1947/8*	*1948/9*	*1949/50*	*1950/1*	*1951/2*
Rotations		See Table III	See Table IV			
FFC	278			264	210	279
DFC	281			270	231	284
DDC	285			260	239	281
LFC	292			266	247	302
DLC	302			267	239	273
Sig. diff.	10·5			N.S.	N.S.	N.S.

TABLE 3

Organic-nitrogen Values in p.p.m. for Plots Growing Cotton in Season 1947/8

Rotation	FFC	DFC	DDC	LFC	DLC
Sampling date					
1947					
28/5	345	360	368	377	395
9/6	363	361	368	395	396
23/7	372	370	370	386	409
23/8	351	339	341	333	345
26/9	311	312	313	315	311
1948					
10/5	266	260	276	275	280

Sig. diff. between rotations on a given date = 20·3.
„ „ „ dates for a given rotation = 21·3.

TABLE 4

Organic-nitrogen Values in p.p.m. for the Three Phases of the Cotton-Fallow-Fallow Rotation during Season 1948/9

Rotation phase	FFC	FCF	CFF
Sampling date			
1948			
8/3	266	239	248
8/4	277	280	263
8/5	262	259	246
12/6	263	257	264
28/6	285	284	280
13/7	286	272	281
28/7	289	285	290
12/8	294	287	290
29/8	313	312	313
16/9	290	279	302
1/10	299	274	290
16/10	290	288	294
30/10	280	277	279
27/11	294	280	283
26/12	297	279	273
1949			
17/1	283	279	276
15/2	269	272	268
5/3	279	230	281
20/3	274	263	269
3/4	274	274	279
16/4	276	269	274
30/4	271	273	274
Sig. diff.	11·2	14·7	12·7

General Features

(i) *Organic nitrogen*

In the light of the statistical treatment and from a general impression of the results already given, a striking feature that emerges is the similarity in the changes in soil organic nitrogen in any single season irrespective of rotation and phase. Equally striking perhaps is the dissimilarity that is evident between seasons.

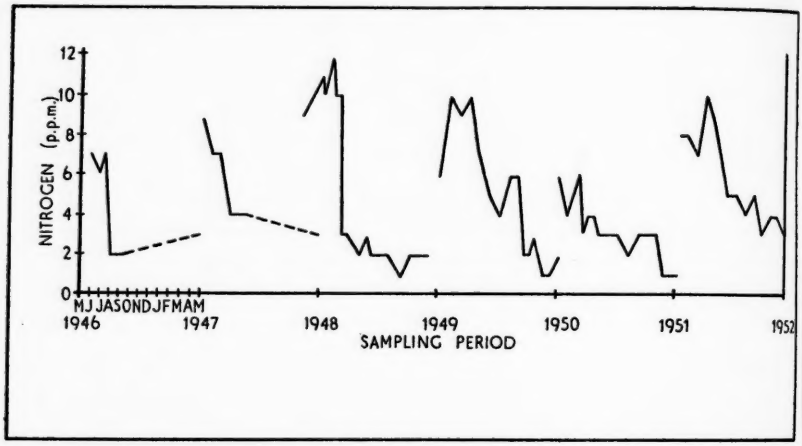

FIG. 1. Showing seasonal variation in nitrate nitrogen in p.p.m. as means of the cotton-phase of all five rotations.

In 1946/7 organic nitrogen in the soil increased from a statistically common value for all five rotations to a value some 60 p.p.m. higher following the rainy period of July and August. A second increase of approximately equal magnitude occurred some time between October and the end of the season in May 1947. Initial sampling of the plots coming into cotton in season 1947/8 showed that the organic-nitrogen content of these plots was approximately equal to that of the previous season's cotton plots at the time of their final sampling. As the extent of the work on the cotton plots in 1946/7 prevented sampling of all rotational phases, and because of the restricted randomization in the field layout, it was not possible at this stage to say whether the apparent continuity in organic-nitrogen level between the two sets of plots over the two seasons was real. Further work to be described later provided indirect evidence to show that the large increase in nitrogen referred to was probably general in the 'Three-Course Rotation'.

During the 1947/8 season there was no increase in organic nitrogen associated with the rainy period of 1947, and as shown in Table 3 a large nitrogen loss was observed later, of the order of approximately 110 p.p.m. for all rotations. This reduced the nitrogen content of the plots to the same order of nitrogen as that which existed prior to the 1946 fixation.

TABLE 5

Season 1948/9. Soil Nitrates in First and Second Foot Soil Samples as Nitrogen in p.p.m. under the Three Phases of the Cotton, Fallow, Fallow Rotation

Rotational phase	FFC	CFF	FCF	FFC	CFF	FCF
Foot	1	1	1	2	2	2
Sampling date						
1948						
March . .	**9**	5	3	3	1	1
April . .	**10**	7	2	**7**	3	1
May . .	**11**	8	3	**7**	3	1
June (i) . .	**10**	9	3	**7**	4	1
(ii) . .	**12**	6	3	**8**	3	1
July (i) . .	**10**	5	3	**8**	2	1
(ii) . .	**10**	8	2	**4**	2	1
Aug. (i) . .	3	8	3	**10**	3	1
(ii) . .	3	7	2	6	6	1
Sept. . .	2	8	1	3	9	1
Oct. (i) . .	3	4	2	5	6	1
(ii) . .	2	4	2	3	6	2
(iii) .	3	5	2	2	7	2
Nov. . .	2	4	2	1	5	1
Dec. . .	2	5	2	1	5	1
1949						
Jan. . .	1	**7**	2	1	**9**	1
Feb. . .	2	**9**	3	1	**11**	2
March (i) .	2	**7**	2	2	**8**	1
(ii) .	2	**9**	2	1	**9**	1
April (i) . .	3	**10**	2	1	**11**	2
(ii). .	1	**10**	2	1	**11**	2
(iii) .	2	**13**	3	1	**10**	2
Sig. diff. between dates . .	2·9	4·0	Not Sig.	2·1	2·7	0·5

The sampling of all phases of rotation 1 (CFF) in 1948/9 was undertaken in an attempt to observe more closely the various gains and losses that had occurred in the previous seasons should they be repeated, and to try and trace their cause. It was felt that rotation 1 with its uniformity of root residues might be simpler in its mode of operation than the other four rotations of the experiment in which two or three types of root residue were subjected to microbiological attack. The investigation commenced in March before the 1947/8 crop was complete, and the results have shown a general picture essentially different from the two previous seasons. Although only results of first-foot soil sampling are given in this paper, the second foot of soil was also sampled and analysed, and there appeared to be a marked uniformity in nitrogen content to a depth of 2 ft. in this soil. A strong similarity in the behaviour of the three rotational phases is also pronounced, but the statistically established phase-date interaction must not be forgotten in considering this similarity. A slight increase in nitrogen occurred in March and April 1948

(except in the cotton phase which just failed to attain significance) followed by a loss of this nitrogen in May. The possibility that leaf-fall, which occurs extensively from February to April, might add organic nitrogen directly to the soil was investigated as a possible explanation of this feature, although in such circumstances the changes should be most marked on the cotton phase. For this purpose successive 1-in. samples from one hole on each phase of the rotation were taken to a depth of 2 ft. and their organic nitrogen and nitrate contents determined. No accumulation of nitrogen was observed in the upper soil layers and the effect of leaf-fall must accordingly be of little consequence. During the remainder of the season an increase in organic nitrogen occurred between June and August 1948 followed by a gradual loss of nitrogen until mid-February 1949 when approximately 45 p.p.m. had disappeared. The first fallow phase, however, continued to lose nitrogen until early March with the rapid disappearance of a further 40 p.p.m. This was rapidly regained and in April 1949 all three phases of the rotation possessed similar nitrogen contents.

The succeeding season 1949/50 bears some resemblance to 1947/8 in that no marked nitrogen increase occurred during the rainy period. In addition a steady decrease in nitrogen content of all plots was observed throughout the whole season which terminated in May 1950 with a rapid loss of 50 p.p.m. It was found that the overall decrease could be adequately represented by a linear regression, the decrease being 0·6 unit per day. Although small, this was significant. The final rapid loss in May was rapidly regained as shown by the first sampling for the season 1950/1; following this recovery, however, there was no marked increase in soil organic nitrogen during the wet months. The season in fact showed no consistent movement in the level of organic nitrogen, but a minimum value was observed in April 1951 which was significantly lower than the peak value found in August 1950. Nitrogen contents were lower throughout this season than had been previously observed during the study.

During 1951/2 nitrogen contents of all plots were higher than during the previous season and more in line with the general level of nitrogen contents observed in the earlier years of the study. The highest observed value was clearly associated with the rainy period and was significantly higher than that recorded in June 1951. A minimum figure observed in March 1952 was not significantly lower than the January figure. A marked fall in organic nitrogen thus took place between December 1951 and early January 1952. This is the earliest time when a minimum nitrogen figure has been recorded in this study.

After six years' completed work a certain amount of evidence has now accumulated against there being discontinuity in the measured nitrogen content of cotton plots due to the seasonal shift in plots. This shift arises from the restricted randomization used in the field experiment (see Crowther and Cochran, 1942). No marked discontinuity has been observed in any season (excluding 1951/2) at the time of the May sampling when the shift occurs. The apparently big difference between the end of 1951 and the beginning of 1952 is best assessed from a study of Fig. 2,

WEEKLY RAINFALL MEANS

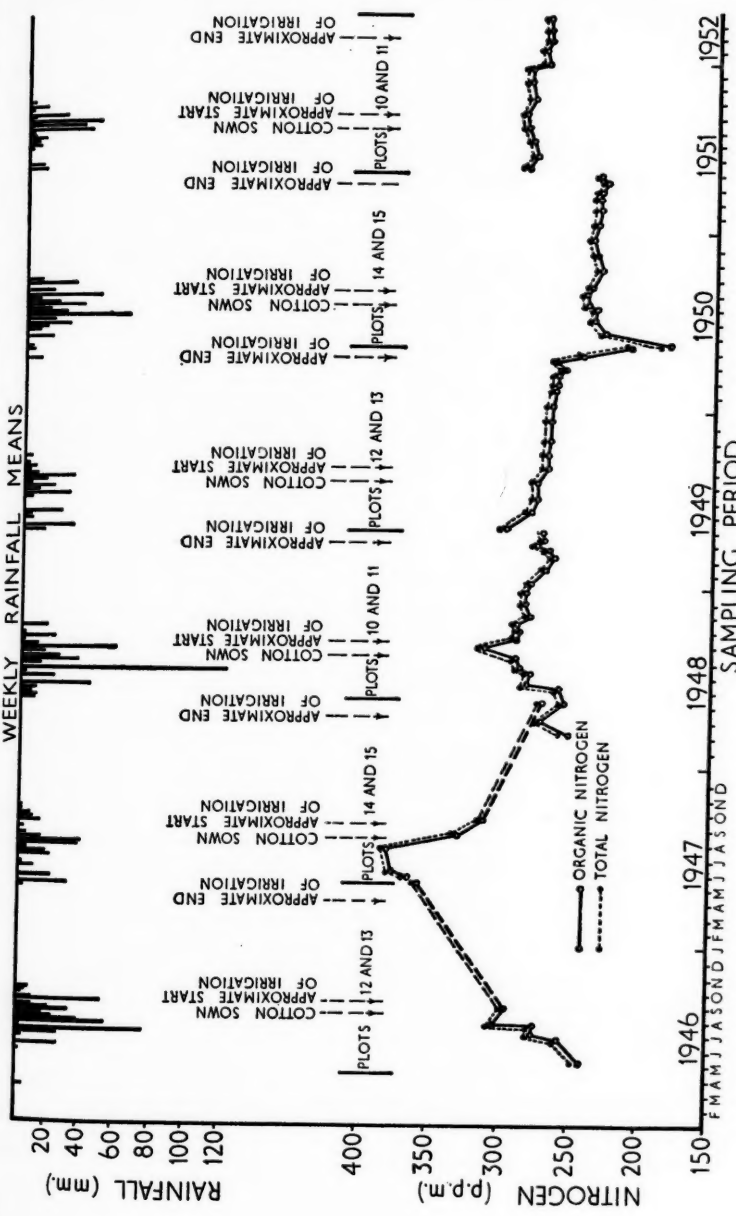
WEEKLY RAINFALL MEANS
RAINFALL (m.)
NITROGEN (p.p.m.)
SAMPLING PERIOD
F M A M J J A S O N D J F M A M J J A S O N D
1946
1947
1948
1949
1950
1951
1952
ORGANIC NITROGEN
TOTAL NITROGEN
PLOTS
COTTON SOWN
APPROXIMATE START OF IRRIGATION
APPROXIMATE END OF IRRIGATION
12 AND 13
14 AND 15
10 AND 11

FIG. 2.

which shows the progressive changes in soil nitrogen as averages of all rotations during the six years investigated.

The possibility exists that the plots concerned in this rotational shift are more erratic in their behaviour with respect to organic nitrogen than the others. In the absence of firm evidence to the contrary, however, the large difference between 1950/1 and 1951/2 cotton plots may be regarded as a general rise in organic-nitrogen content in all plots, and as being opposite in nature to the rapid loss that occurred between

TABLE 6

*Seasonal Means of Nitrates as Nitrogen in p.p.m. of Soil and Cotton Yields in Kantars per Feddan (kpf)**

Rotation	FFC		DFC		DDC		LFC		DLC	
Seasons	*Yield kpf*	NO_3 N *p.p.m.*	*Yield kpf*	NO_3 N *p.p.m.*	*Yield kpf*	NO_3 N *p.p.m.*	*Yield kpf*	NO_3 N *p.p.m.*	*Yield kpf*	NO_3 N *p.p.m.*
1946/7 .	2·38	8	2·21	3	1·58	2	2·84	7	2·43	4
1947/8 .	2·22	6	2·95	4	2·13	2	3·80	13	3·29	4
1948/9 .	3·91	5	2·89	..	2·67	..	4·28	..	4·04	..
1949/50 .	3·59	5	3·73	5	2·56	2	4·14	8	4·15	4
1950/1 .	6·40	3	5·58	3	3·03	2	7·43	4	6·25	3
1951/2 .	3·64	5	3·24	4	2·01	3	4·84	11	4·12	5
Long term Means†	4·66	9	4·30	8	3·10	4	4·95	15	4·55	8

* 1 kantar = 312 lb. of unginned cotton; 1 feddan = 1·038 acres. † Involving years 1934–48.

seasons 1949/50 and 1950/1. Prior to May 1951 no discontinuity occurred during the period of rotational shift of the plot pairs. Further, the three phases of rotation 1 (CFF), distributed as they are over all the plots of the experiment, showed closely similar behaviour. It seems, therefore, very likely that the relative changes in nitrogen content for the whole experimental area during one season may be conveniently illustrated by studying just one group of plots.

(ii) *Nitrate nitrogen*

Soil-nitrate figures under three-course rotational cropping in the Sudan Gezira are in distinct contrast to the figures for soil organic nitrogen, since they show a marked dependence on rotation. This dependence is most clearly seen during the earlier sampling months of each season, when, it is assumed, the rainy period induces bacterial activity and consequent build-up of nitrates in the soil. The tailing-off of soil-nitrate content in the later months due to crop uptake of nitrate nitrogen and other possible causes makes the relative rotational effects less obvious.

Rotation 4 (CLF), for each year studied, shows a much higher soil-nitrate content than the remainder of the rotations, and the effect of this on ultimate cotton yields is very evident, as shown in Table 6.

Distinction between the remaining rotations, however, is by no means so clear. In some years, for example, yields of cotton under rotation 1 (CFF) are greater than under rotation 5 (CDL), but in the majority of the years actually studied the reverse is true. Soil nitrates, however, are

greater under rotation 1 (CFF) than 5 (CDL). On the basis of nitrate content alone rotation 5 appears comparable to rotation 2 (CDF), whereas on a yield basis it is persistently better than it. This is presumably due to the leguminous lubia providing readily nitrifiable material to the subsequent cotton crop, and thereby offsetting the detrimental effects of the dura (Conrad, 1928). The influence of dura root residues can be observed in the progressively decreasing nitrate contents of rotations 1 to 3 (CFF, CDF, CDD), which effect is also to be seen in the cotton yields of the rotations. It is interesting to note, however, that rotation 2 (CDF) in 1949/50 gave a higher yield than rotation 1 (CFF), although the mean nitrate content for the whole season was the same for the two rotations. Examination of the detailed nitrate nitrogen figures for 1949/50 indicated that, unlike the other years studied, rotation 2 possessed soil nitrates somewhat higher than rotation 1 at the beginning of the season. The same relative yield levels for these two rotations are also to be observed during season 1947/8, but there is no similar correspondence of soil nitrates. Field observations, however, have shown that during that season, rotation 1 suffered very badly from waterlogging.

Table 5 shows in detail the nitrate figures for first- and second-foot soil samples of all phases of rotation 1 during season 1948/9. The value of fallowing in building up nitrate reserves is very evident. The end of the second fallow following cotton exhibits an appreciable nitrate accumulation to a depth of 2 ft. Of very great importance is the early appearance of this soil nitrate. The data presented indicate that the main nitrate reservoir in the soil has been replenished about five months before the rainy season is due.

Discussion

Throughout the investigation the total-nitrogen figures (i.e. organic nitrogen plus nitrate nitrogen) have shown changes which have closely followed those of organic nitrogen. Nitrate fluctuations have made little contribution to the magnitude of these changes, and it would appear that the mineralized and the organic fractions of nitrogen in this soil do not function in close interdependence.

Much importance has been attached to the study of soil nitrates in the Gezira as a probable explanation of the large fluctuations in annual cotton yields that occur. These fluctuations have been found by Crowther (see Tothill, 1948) to be directly correlated with rainfall during certain periods of the year. Degree of nitrification, however, did not provide a direct explanation of this phenomenon. Thus soil nitrates, although readily correlated with cotton yields between various rotations within one season, show no association with variations in annual rainfall or annual yield changes. Jewitt (1950) has established in a recent survey of past work that the rainfall/cotton yield relationship definitely does not function by way of increased soil nitrate at sowing time at least in top-foot soil. He actually proved that the reverse was true, namely, that heavy rain just previous to sowing decreased top foot nitrates by leaching to a greater depth.

A study of the data presented in this paper shows that increased

nitrate in top-foot soil takes place much earlier than the rainy period, although a further increase can be observed following rain. Thus in each year of study an appreciable nitrate accumulation is already found in the soil in May well before the beginning of the main rainy period. This fact is best illustrated by seasons 1948/9 and 1949/50. The early rains of 1948/9 and 1949/50 were recorded as:

1948		*1949*	
May 21	4·4 mm.	May 13	15·4 mm.
,, 24	0·8 ,,	,, 15	27·2 ,,
,, 26	3·5 ,,	,, 20	3·8 ,,
,, 28	7·3 ,,	,, 21	3·6 ,,

After eight months of continuous drought, showers of such magnitude do little more than bring a very temporary respite to the heat which is characteristic of these months in the Sudan. Their wetting effect on the soil is negligible, and all moisture evaporates into the very dry air within a couple of hours. Table 5 (season 1948/9), however, indicates that there existed as early as March of that season an accumulated soil-nitrate content which did not appreciably increase even during the later rainy months of June and July. The feature is observable in the cotton phase to a depth of 2 ft. and also in the top foot of the second fallow phase. It is also noticeable in the top 2 ft. of the second fallow phase during the early part of 1949. This stage of course represents the land that is due to come under cotton in 1949/50, and the figures therefore provide a continuity of observation from 1948/9 into the 1949/50 cotton plots under rotation 1 (CFF). Considering then rotation 1 during this latter season, it is clear that the nitrate available in the soil had started to accumulate from January 1949.

At present no explanation of this phenomenon is offered, since available data are scanty. There is sufficient indication, however, from results to date, to show that the rainy months in the Sudan may not be the main period of nitrate accumulation, and that rainfall as such may not be the chief agency in inducing nitrification. The possibility that nitrate accumulation can occur on the bare dry fallows is in accord with the work of Hardy (1946) who observed this phenomenon during the dry season in Trinidad, when the available moisture content of the soil was reduced to within the capillary range. Griffith (1951) also records nitrate accumulation on bare fallows in Uganda.

Changes too in the organic-nitrogen content of Gezira soil are not obviously associated with rainfall conditions. It will be seen from Fig. 2 that significant increases in organic nitrogen occurred both during and prior to wet periods. The very large increase in nitrogen that occurred in 1946/7 apparently took place in two stages, each approximately of the order of 60 p.p.m. This represents a phenomenal increase in soil nitrogen, the amount of nitrogen used by the cotton crop being comparatively small. The correspondingly large loss of 120 p.p.m. of nitrogen observed in 1947/8 cannot be explained in terms of uptake by the crop, which was equivalent to 11 p.p.m. reckoned on top-foot soil.

Large fluctuations in nitrogen content of soil were recorded by Wilsdon and Ali (1922) for irrigated tracts in India. They could not correlate these changes with any known available data. Diamond (1937), working on Nigerian soil, reported fluctuations from day to day and claimed that the range of fluctuations was marked by a seasonal influence in the spring. In the present study the possible controlling influence of weather conditions has been suspected.

Under Gezira conditions rapid disappearance of nitrogen occurs when the soil nitrogen content is already low. Rapid loss is succeeded immediately, however, by an equally rapid nitrogen recovery of about the same magnitude. The period of the year when this phenomenon occurs—February to May—is one of hot desiccating winds when the bare soil is strongly heated by insolation. Under these conditions soil moisture is at a minimum, so that if the established increases in organic nitrogen are evidence of fixation of atmospheric nitrogen, then nitrogen-fixing organisms must be capable of functioning under the exacting conditions that obtain. Greene (1932) found that azotobacter in Arizona soils have adapted themselves to a higher temperature environment, and consequently are able to fix nitrogen at higher temperatures than cultures of the same organism from temperate regions. Although Greene's experimental conditions were perhaps less exacting than those which prevail in the Gezira, some support for his results is provided by the present study. The accumulation of nitrate nitrogen as early in the year as January is positive evidence that some form of activity is operative in this soil during the dry season.

The actual mechanism of loss and the form in which nitrogen is lost from Gezira soil is still obscure. Several possibilities present themselves in explanation. It is improbable that the loss is due to downward leaching for loss has been observed in fallow plots during the dry season, and because no large corresponding accumulation of organic nitrogen in the lower soil layers has been observed. The extreme impermeability of the soil, furthermore, does not favour the possibility. Jewitt (1945) has obtained loss of ammonia from added fertilizers in this highly alkaline soil, but failed to detect liberation of ammonia from soil alone. The evolution of nitrogen peroxide from soils has been reported, but the degree to which this seems to occur does not offer a likely explanation of the very large losses that have been observed with Gezira soil. Loss of elemental nitrogen and nitrous oxide following upon denitrification must be considered especially in view of the claim by Kriegel (1944) that nitrous oxide is one of the most abundant constituents of soil air. Arnold (1954) emphasizes that loss of nitrous oxide from soil would be expected to be a seasonal phenomenon and that it involves the mineralized nitrogen fraction under anaerobic conditions. Nitrogen loss in Gezira soil is, however, associated with the organic fraction. This may only be reconciled with Arnold's findings if nitrification and denitrification have occurred in succession at a rate fast enough to avoid detection—possibility clearly to be borne in mind, but one not likely to provide a favourable solution when other environmental factors are considered.

That observed losses are apparent only, being conversion to 'non

Kjeldahlisable' nitrogenous forms, provides another explanation which merits further study.

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A MINERALOGICAL STUDY OF WEATHERING AND SOIL FORMATION FROM OLIVINE BASALT IN NORTHERN IRELAND

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Abstract

The composition of a soil profile derived from olivine basalt in Northern Ireland is described with the assistance of a series of diagrams of the cumulative curve type incorporating mineralogical and particle size data. The weathering sequence of primary minerals in the basalt is olivine, labradorite, augite. Olivine alters to vermiculite and labradorite to kaolin. The soil resisted all attempts to achieve complete dispersion and its high state of aggregation is considered to affect its physical properties. The presence of quartz is attributed to glacial contamination.

THE mineralogical study of soils for many years lagged behind that of igneous and sedimentary rocks for the reason that soils are not readily characterized under the petrological microscope. In view of this restriction investigations were confined to the sand fractions as in the work of Hendrick and Newlands (1923) and Hart (1929) who were nevertheless able to draw certain conclusions as to the relationships between some Scottish soils and the bedrock from which they were ultimately derived.

With the introduction of X-ray, electron diffraction and differential thermal methods of analysis, the emphasis in soil mineralogy has swung to the other extreme of the particle size scale, the colloidal fraction. Jackson *et al.* (1948) and Fieldes and Swindale (1954) have summarized the clay mineralogy of soils in North America and Australasia, and published with their results generalizations about the sequence of weathering in the colloidal fraction. For example Jackson *et al.* concluded that the stage reached in the weathering sequence is partly a function of particle size, that is, the fine clay in a soil is in a more advanced stage of weathering than the coarse clay. Stephen (1952, *a* and *b*) extended this principle by examining both sand and clay fractions of soils derived from various igneous rocks in the Malvern Hills. He found that the sand was composed dominantly of mineral fragments from the underlying rock and that in progressively finer grades there were greater proportions of secondary minerals.

As well as establishing the weathering history in a soil profile, mineralogical data may be used in accounting for some of its physical and chemical properties. In Northern Ireland extensive soils derived from basalt have been classified by Brown (1954) as brown earths on account of their high content of exchangeable cations and their well-developed crumb structure. The abundance of sesquioxides and bases he considered result from the weathering of ferro-magnesian minerals which constitute about half of the rock. He also noted that the soils have very high cation exchange capacities which is true even where the clay content is low.

In this study the total mineralogy of a soil profile similar to one described by Brown is described in some detail. Successively more vigorous methods of dispersion were used to break up the aggregates, after each treatment the soil was divided into seventeen particle size groups, and quantitative mineralogical analyses were made of each. The results are represented in compound diagrams of the cumulative curve type constructed to show the particle size distribution of the component minerals in each of three soil horizons and in the weathered crust surrounding rock fragments.

Field Data

The Antrim Plateau is an extensive upland region in north-eastern Ireland formed from basaltic and tholeitic lavas of Tertiary age outcropping over a total area of 1548 sq. miles; it is thus the largest region of basic igneous rocks in the British Isles. The stratigraphy of the lavas has been described by Patterson (1955) who recognized three groups of flows separated by inter-basaltic horizons representing long periods of weathering under a hot, humid climate. Whether the upper lavas were similarly affected is unknown, since during the Quaternary period the plateau was scoured by glaciers leaving large areas almost devoid of superficial deposits.

Such was the case at Craigpark quarry 1½ miles east-south-east of Bushmills where samples for this study were collected. The soil profile has developed from shattered olivine basalt in an excessively drained site (20° slope). At the surface is a spongy black moder with abundant roots. Below 5 in. the structure becomes less distinct although there is still a high proportion of organic matter. At a depth of 12 in. the colour changes to orange-brown and angular stones become increasingly frequent until shattered basalt is reached at about 20 in. The fragments of rock appear quite fresh, except for a dense ferruginous skin a few millimetres thick at the outer margin.

Laboratory Methods

Dispersion. Soils derived from basic igneous rocks are well known for their high degree of aggregation, and the method of dispersion by shaking in distilled water to which a few drops of NH_4OH have been added was found ineffective. Mackenzie's (1954) method for removing free iron oxides with sodium hydrosulphite was employed followed by digestion for several days in hydrogen peroxide over a water bath, and a final treatment with hydrosulphite.

Separation into particle size groups. As well as making a detailed mechanical analysis, the object was to obtain samples of different particle size groups for mineralogical analysis. For the sand fractions this was done simply by sieving, but the exhaustive decantations necessary to achieve complete separation of the silt and clay fractions were not considered worth while. Instead cumulative samples of clay and silt were obtained by the pipette method, their minerals analysed and their quantities in each particle size group found by subtraction.

The coarse sand fractions were separated by passing the dispersed soil

through a 0·2 mm. mesh sieve and dividing the residue by further sieving into four groups: 2–1 mm., 1–0·5 mm., 0·5–0·3 mm., and 0·3–0·2 mm. The remaining suspension was transferred to a 500 ml. settling cylinder from which the finer grades were siphoned. Samples were thus obtained of fractions $<30\mu$, $<20\mu$, $<10\mu$, $<5\mu$, $<3\mu$, $<2\mu$, $<1{\cdot}5\mu$, $<1\mu$ and $<0{\cdot}5\mu$ equivalent spherical diameter (e.s.d.). The fine sand fractions were isolated by repeatedly decanting finer material; they were subdivided by sieving into four groups: 0·2–0·15 mm., 0·15–0·1 mm., 0·1–0·05 mm., and 0·05–0·03 mm.

Mineralogical analysis. The minerals of the fresh rock were determined under the petrological microscope and a quantitative analysis was made from eight thin sections by measuring the intercepts of every mineral in a hundred random fields. Minerals present in the sand fractions of the soil were estimated microscopically by counting several hundred grains of each particle size group. The silt and clay minerals were analysed with X-rays using filtered cobalt radiation; qualitative identifications of the clays were made with 'pressure aggregated' specimens (Mitchell, 1953), while quantitative analyses of silts and clays were made by grinding the sample to a fine powder with KCl as an internal standard, and comparing the intensities of the diffraction lines on rotated powder photographs with those of standard mixtures of the component mineral and KCl (Mitchell, in preparation). Clay minerals present in the fresh rock were extracted by crushing a sample until all had passed through a 0·15 mm. mesh sieve and shaking overnight in a 0·01 N solution of Na_2CO_3 (Caillère *et al.*, 1954). The suspension of clay-sized particles was then siphoned from a depth of 10 cm. after settling for 8 hours in a glass cylinder.

Petrography of the Olivine Basalt

The rocks exposed in the Craigpark quarry are olivine basalts of the plateau magma type (Patterson, 1955). The ophitic texture is dominated by randomly oriented felspar laths penetrating all but the olivine

TABLE 1

	% *volume*	*S.G.*	% *weight*
Labradorite .	44·8	2·71	39·5
Augite . .	29·6	3·30	31·6
Olivine . .	12·3	3·33	13·3
Magnetite. .	4·5	5·17	7·5
Vermiculite .	5·7	2·80	5·2
Kaolin . .	1·9	2·63	1·6
Sphene . .	0·7	3·50	0·8
Apatite . .	0·5	3·20	0·5

phenocrysts, which are therefore shown to have crystallized first. The mineralogical composition is given in Table 1.

Labradorite is present wholly as laths 0·5 to 0·05 mm. long with a length to breadth ratio of about 5:1. In sections cut normal to 010 and showing combined albite and Carlsbad twinning the two extinction

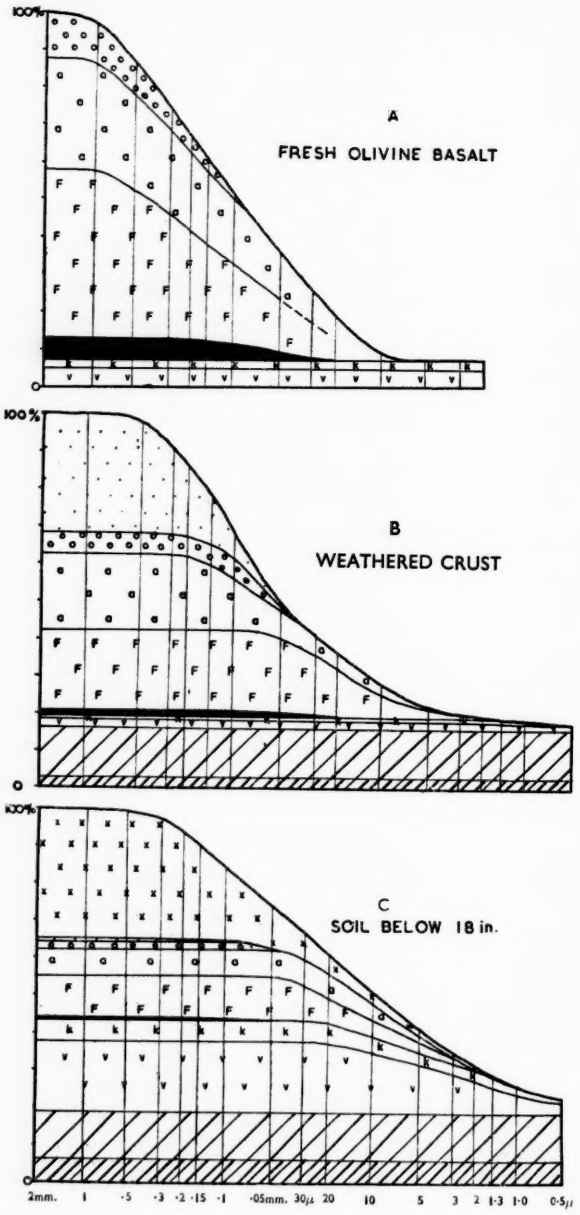
100%
A
FRESH OLIVINE BASALT
100%
B
WEATHERED CRUST
100%
C
SOIL BELOW 18 in.
2mm. 1 ·5 ·3 ·2 ·15 ·1 ·05mm. 30μ 20 10 5 3 2 1·3 1·0 0·5μ

FIG.

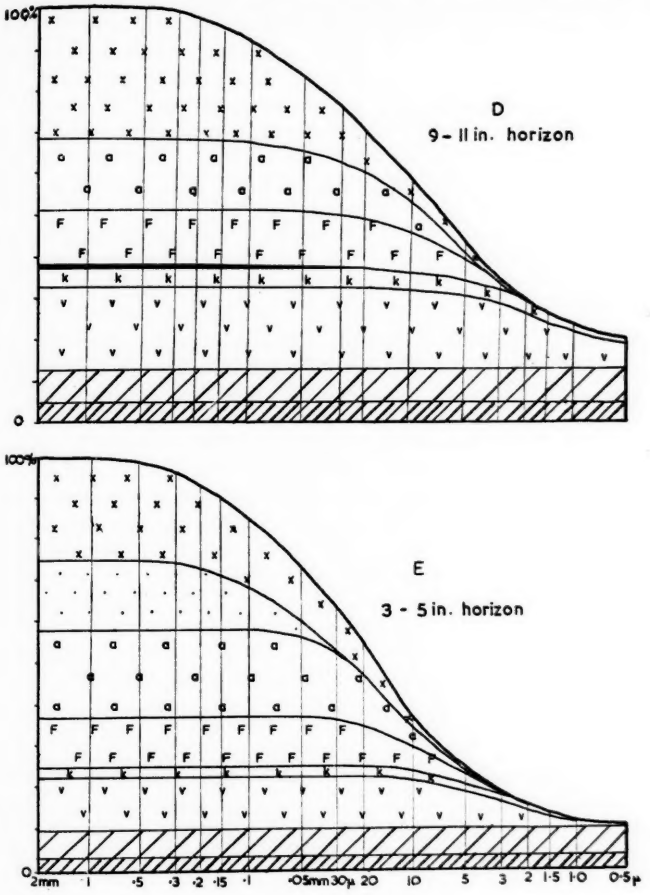

FIG. 1. Cumulative curve diagrams illustrating mineralogical and particle-size data of olivine basalt, its sub-aerially weathered crust and three soil horizons.

angles were measured and the composition was shown to be An_{57} Ab_{43} (Winchell, 1948). Augite occurs as small purplish brown grains about 0·2 mm. in diameter, and also in allotriomorphic crystals as large as 2 × 1 mm. ophitically penetrated by the labradorite laths. Locally irregular patches of augite show an olive-green alteration visible in the unmagnified section. Olivine is found in prismatic phenocrysts as large as 1 mm. in diameter and as small grains in the ground-mass. It is optically positive and 2V being between 80° and 85° the approximate composition is given as Fo_{70} Fa_{30} (Winchell, 1948). Alteration along curved fractures has produced a yellow-brown finely crystalline substance.

The total amount of secondary minerals was estimated optically as 7·6 per cent. They were identified as vermiculite and kaolin present in the proportion vermiculite:kaolin = 3:1, and the actual quantities of each mineral were reached by dividing 7·6 per cent. in this ratio.

The Weathered Crust

Fragments of basalt in the lower part of the soil profile have a highly ferruginous weathered crust about 2·5 mm. thick. In thin section it was divisible into two zones, an inner softer layer about 1·5 mm. thick and a much denser and darker outer skin. Through both zones remnants of olivine and augite crystals can be seen. In one section a very thin (0·01 mm.) undulating band of ferruginous staining was present in the fresh rock at a distance of about 4 mm. from the outer margin; it probably represents an early stage in the formation of a plane of exfoliation.

The crust was scraped from a fragment of basalt, dispersed by removing its free sesquioxides with sodium hydrosulphite (Mackenzie, 1954) and separated into particle size groups for mineralogical analysis (Fig. 1).

Composite sand grains are described as fresh or weathered basalt according to how readily they could be crushed with a needle. The distinction was confirmed when grains of each type were powdered and their X-ray photographs taken; felspar, augite, and olivine are present in both samples, but in the weathered grains the amount of augite is increased at the expense of the other two minerals. The smallest composite grains are 0·03 mm. in diameter.

Sand-sized grains of olivine gave strong diffraction lines characteristic of a well-crystallized mineral, a 14 kX spacing was also present which was not expanded by treatment with glycerol, but after heating for half an hour at 600° C. it collapsed to 9·8 kX indicating vermiculite. Olivine grains range in size from 0·3 to 0·03 mm. with a greatest frequency between 0·1 and 0·05 mm. (Fig. 1B). The largest augite fragments are spongy relics of allotriomorphic crystals 0·5 mm. in diameter. X-ray powder photographs of the crushed grains show that the ophitic laths of felspar have weathered to a kaolin, since the very strong felspar spacing of 3·19 kX is absent and instead are 7·06 and 4·45 kX representing a kaolin. The relative stability of augite is indicated by the fresh appearance and sharp edges of grains. Small crystals of magnetite persist unaltered from the fresh rock.

Labradorite is seen as angular glassy grains in the very fine sand fraction (0·05 to 0·02 mm.) and comprises 70 per cent. of the silt (20 to 2μ). There is little fine silt or clay present, only 6 per cent. of the sesquioxide free crust being less than 5μ and 2 per cent. less than 1·5μ e.s.d. (Fig. 1*b*). The clay fraction is composed mainly of material amorphous to X-rays, but in an aggregate photograph of the fraction less than 1μ spacings of 14·2, 4·58, and 3·51 kX were interpreted as vermiculite, while small amounts of kaolin and illite may also be present.

Composition of the Soil

Three samples of the shallow profile exposed in the Craigpark quarry were taken, from 3 to 5 in., 9 to 11 in., and from below 18 in. Mineralogical analyses were made in three stages of dispersion: (1) after shaking in distilled water to which a few drops of NH_4OH had been added; (2) after removing free iron oxide with sodium hydrosulphite; and (3) after treatment with hydrosulphite and hydrogen peroxide.

TABLE 2

	2–1 *mm.*	1·0–0·5 *mm.*	0·5–0·3 *mm.*	0·3–0·2 *mm.*	0·2–0·15 *mm.*	0·15–0·10 *mm.*	0·10–0·05 *mm.*	0·05–0·02 *mm.*	20–10 μ	10–5 μ	5–3 μ	3–2 μ	1·5–1 μ	0·5 μ
18-in. horizon														
(i) Per cent. loss on ignition. .	24	26	23	24	17	26	26	22	32	32	35	38	40	43
(ii) Per cent. haematite after heating at 750° C.	8	n.d.	10	n.d.	n.d.	5	10	n.d.	8	n.d.	n.d.	10	10	5
3–5 in. horizon														
(i) Per cent. loss on ignition. .	40	42	47	n.d.	n.d.	40	24	20	30	30	37	n.d.	32	38

	3–5 in.	9–11 in.	18 in.
Per cent. loss on treatment with H_2O_2 . .	14·3	12·7	7·1

In the least-dispersed state less than 10 per cent. of the soil is present in particles smaller than 2μ e.s.d., while between 68 and 78 per cent. of sand-sized material was recorded (Fig. 3), the grains of which contained erratic quartz, fragments of augite and felspar derived from the basalt, clay minerals, and a proportion of free sesquioxides and organic matter amorphous to X-rays. A sample of each particle size group was ignited to 750° C. and the percentage loss determined (Table 2). It should be pointed out that the loss on ignition cannot be equated with the amount of organic matter, since on heating to 750° C. vermiculite loses 14·3 per cent. of its original weight (Walker, 1951), also water is lost by hydrated amorphous iron oxides upon conversion to haematite. The percentages of haematite in some of the ignited samples are also recorded in Table 2.

Treatment with sodium hydrosulphite decreased the amounts of coarse sand while the proportions of clay rose by as much as 18 per cent. (Fig. 3). But much of the sand still consisted of aggregates which appeared to represent basalt in varying stages of decay.

Almost complete dispersion was achieved when the soil was treated

with sodium hydrosulphite and hydrogen peroxide. Less than 6 per cent. was retained by the 0·2 mm. sieve while the clay increased to between 16 and 32 per cent. (Fig. 3). However, vermiculite and kaolin were recognized in the silt fraction showing that there was still some aggregation.

The cumulative curves (Fig. 1 C, D, and E) illustrate the breakdown of primary minerals by showing their particle size distribution in the basalt

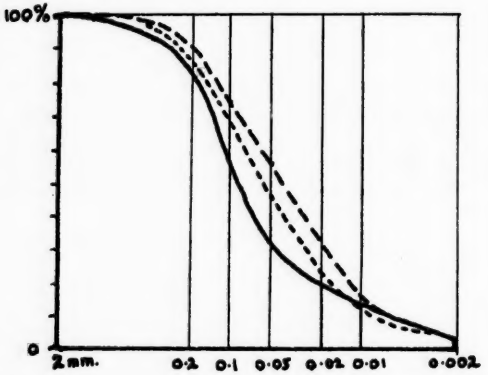

FIG. 2. Cumulative curves of only the quartz in the three soil horizons.

and in each zone of weathering. Olivine is found only in the sand fractions of the lowest horizon, augite and labradorite, however, are common in the sand and silt fractions throughout the soil. The ratio of augite to labradorite increases from 0·78 below 18 in. to 1·75 in the surface horizon; the ratio is also a function of particle size, decreasing in the fine silt fractions where the smallest fragments of labradorite detected (3 to 2 μ) are smaller than those of augite (5 to 3 μ).

The quartz is considered to be either glacial or aeolian contamination or the remnant of a sedimentary formation, e.g. of Pliocene age, that formerly covered this part of Ireland. Cumulative curves of only the quartz in each horizon (Fig. 2) show that there is a wide range of particle sizes with a broad mode in the fine sand fraction, favouring glacial rather than aeolian transport. Aeolian deposits (löess) have more than 50 per cent. of their particles between 50 and 10 μ diameter (Pitcher *et al.*, 1954). Some of the quartz grains are of 'millet seed' type, being nearly spherical and having a smooth polished surface, others are equally rounded but have a frosted surface frequently stained with haematite; both kinds of grain could be inherited from the New or Old Red Sandstones deposited under desert conditions. The many angular grains of quartz and quartzite may be derived from other sandstone formations or from the metamorphic rocks of north-west Ireland or Scotland. The proportion of quartz in the profile increases slightly with depth from 26 per cent. at the surface to 35 per cent. below 18 in.; the smallest grains are between 1·5 and 1 μ e.s.d. (Fig. 1).

TABLE 3

TABLE 3

Summary of Mineralogical analyses (weight per cent.)

	Rock fragments	*Labradorite*	*Augite*	*Olivine*	*Magnetite*	*Apatite*	*Sphene*	*Vermiculite*	*Kaolin*	*Extractable* Fe_2O_3	*Extractable* Al_2O_3
Basalt . .	..	39·5	31·6	13·3	7·5	0·5	0·8	5·2	1·6	..	..
Weathered crust .	32·0	21·4	20·0	6·0	1·6	..	..	1·0	2·0	13·2	2·8
18 in. horizon .	1·6	14·3	11·1	3·2	1·6	..	..	30·0	8·6	20·1	9·5
9–11 in. horizon .	..	19·8	25·1	..	1·2	..	..	29·3	6·6	11·7	6·3
3–5 in. horizon .	22·6	16·0	28·0	..	..	..	..	16·9	3·1	9·1	4·3

TABLE 4

Chemical Interpretation of Mineralogical Data

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O^+	TiO_2	P_2O_5	MnO	H_2O^-	
Basalt . . .	44·7	12·8	6·6	14·6	10·6	6·2	1·8	0·2	1·6	0·4	0·2	0·3	..	100·0
Ditto, Patterson (1955) .	45·93	15·22	3·06	9·26	10·30	8·55	2·63	0·19	1·68	1·54	0·28	0·18	0·89	99·71
Weathered crust .	40·8	14·5	18·2	7·5	8·0	7·9	1·6	0·2	0·9	0·3	0·1	..	..	100·0
18 in. horizon .	30·2	21·7	23·0	4·8	10·0	2·1	0·7	..	7·3	0·1	..	0·1	..	100·0
9–11 in. horizon .	37·2	18·9	14·5	1·4	10·4	2·9	1·0	0·1	7·1	0·2	..	0·3	..	100·0
3–5 in. horizon .	40·7	16·1	11·6	10·5	9·9	4·3	1·4	0·1	4·6	0·4	..	0·4	..	100·0

Source of Analyses

Labradorite: $Ab_{50}An_{50}$ from Lewisian gneiss (Guppy and Thomas, 1931, *Analysis* 572, p. 144) was adjusted to $Ab_{43}An_{57}$.
Augite: Enstatite augite from Mull pitchstone (ibid., *Analysis* 580, p. 146).
Olivine: $Fo_{70}Fa_{30}$, i.e. $(Fe\,SiO_4)_{0\cdot3}\,(Mg\,SiO)_{0\cdot7}$.
Magnetite: $Fe_2O_3.FeO$.
Apatite: $Ca_5F(PO_4)_3$.
Sphene: $Ca\,Ti\,SiO_5$.
Vermiculite: $22\,MgO.5Al_2O_3.Fe_2O_3.22\,SiO_2.40\,H_2O$ (Gruner, 1934).
Kaolin: $Al_2\,Si_2O_5\,(OH)_4$ (Brindley, 1951).

Fragments of fresh and partly weathered basalt are common in the uppermost soil horizon, but are rare at depth (Fig. 1). Grains were sectioned and seen to have the mineral content and ophitic texture of the fresh rock.

Vermiculite and kaolin are the only clay minerals and in fractions between 2μ and 0·5μ are present in the ratio vermiculite:kaolin = 7:3; in the finest clay, however, vermiculite is even more predominant showing that the single crystals of vermiculite are smaller than those of kaolin. Both minerals are found in aggregates as large as 20μ (Fig. 1). The kaolin mineral was identified as fireclay on account of its strong 4·51 kX line (020) merging in the X-ray photograph into a band of scattering between 4·5 and 3·8 kX. The 001 and 002 lines (7·18 and 3·58 kX) are sharp indicating that metahalloysite is not present (Brindley, 1951). Vermiculite was identified by the very strong reflection from its basal spacing of 14·2 kX, the lattice was not expanded by treatment with glycerol, but upon heating for half an hour at 600° C. interlayer water is irreversibly lost and a talc-like structure is formed with a 001 spacing of 9·6 kX (Walker, 1951).

Geochemical Interpretation of Mineralogical Data

The mineralogical composition of the olivine basalt, its weathered crust, and the three soil horizons are listed in Table 3. Following the method suggested by Whitten (1953) the data are redetermined in Table 4 as chemical analyses.

In the soil horizons the erratic quartz has been overlooked, the amounts of the remaining minerals being recalculated to 100 per cent.

An analysis of olivine basalt from the same site by Patterson (1955) is included for comparison.

Discussion

Soils derived from basic igneous rocks have been studied by Brown (1954) and McAleese (1954) in County Antrim, by Glentworth (1944) in Aberdeenshire and by Mitchell and Jarvis (1956) in Ayrshire. Their greater natural fertility, as compared with geographically associated soils derived from other parent materials, is considered by these authors to be

TABLE 5

Horizon	*0–12 in.*	*12–18 in.*	*18–22 in.*
Per cent. clay. . .	15·3	9·8	6·5
Per cent. organic carbon .	5·4	2·3	0·8
Exchange capacity; me/100 g. soil. . .	43·4	32·8	30·1

due to the presence of bases in easily weathered silicate minerals, the formation in the soil of vermiculite and montmorillonite which have high cation exchange capacities, and by their pronounced crumb structure.

Mitchell and Muir (1937) commented on the high exchange capacities of soils with small clay contents developed from basic igneous rocks in north-east Scotland. No chemical investigations have been made on the profile from Craigpark, but data from a similar soil at Slemish, 26 miles

to the south-east, are quoted in Table 5 (Brown, 1954). It will be seen that if the cation exchange is caused solely by the clay fractions, they must be composed of a mineral with an abnormally high exchange capacity, e.g. 463 me. per 100 g. of clay in the 18 to 22 in. horizon.

Hart, Mitchell, and Muir (unpublished) attributed the high exchange capacity of a soil derived from gabbro to sand and silt-sized crystals of vermiculite contributing to the exchange reaction. However, this explanation is discounted in the case of the Craigpark profile, since uncrushed samples of weathered olivine gave smooth X-ray diffraction lines of vermiculite, where silt-sized crystals would have produced spotty lines. It is thought that the presence of clay minerals in the silt fractions is due to imperfect dispersion, a conclusion also reached by McAleese (1954).

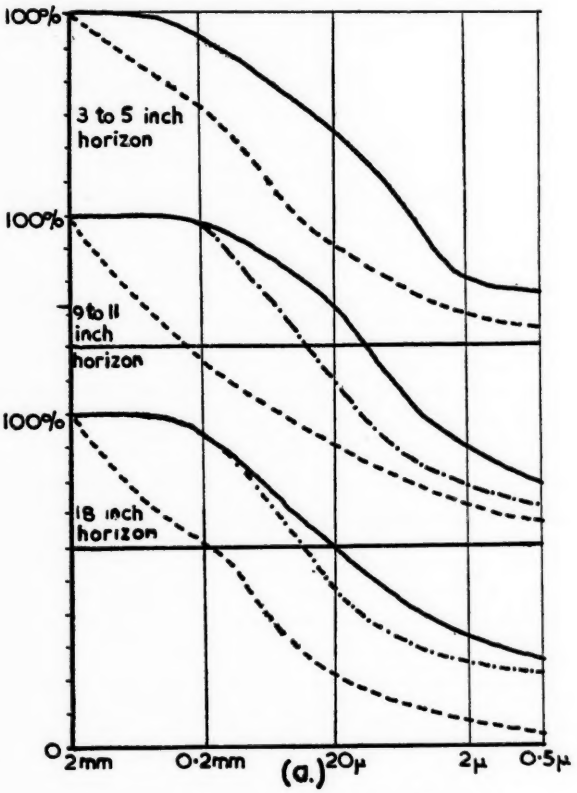

FIG. 3*a*. Cumulative curves of soil horizons

– – – – dispersed with ammonia
–·–·– dispersed with sodium hydrosulphite
——— dispersed with sodium hydrosulphite and hydrogen peroxide

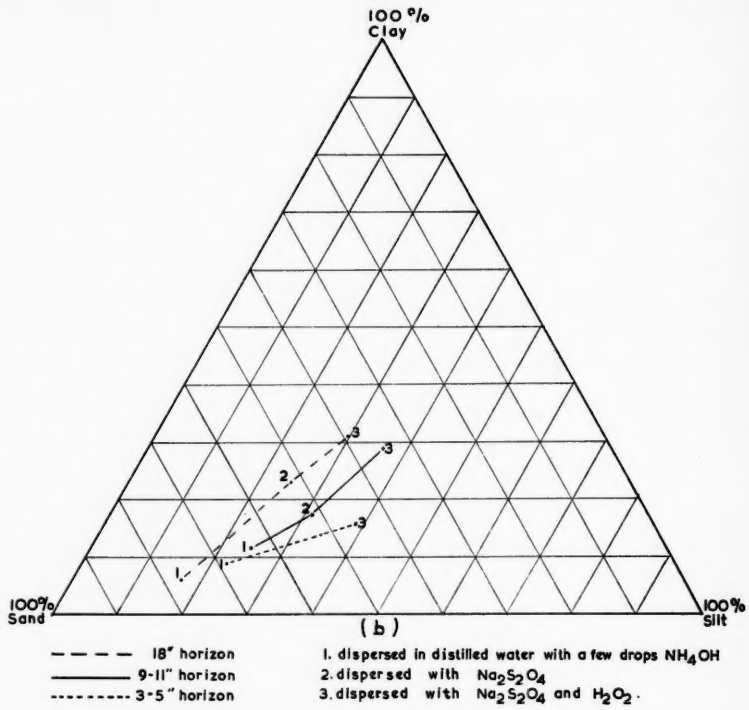

FIG. 3*b*. Mechanical analyses of the three soil horizons, illustrating the change in texture within the profile, and showing the changes in mechanical composition after different methods of dispersion.

The significance of the aggregation of clay into silt and sand-sized grains is that it gives the soil the structure and working properties characteristic of sandy textures, while retaining the high cation exchange capacity of soils rich in clay. The lowest horizon is the most aggregated; Fig. 3 shows how its clay content of 5·6 per cent. after shaking in a dilute solution of NH_4OH rises to 30·6 per cent. after treating with $Na_2S_2O_4$ and H_2O_2 altering the texture from a loamy sand to a clay loam. It is also seen that the proportion of the aggregation caused by organic matter is greater in the 9 to 11 in. horizon than from below 18 in., suggesting that it rises in the profile.

The presence of quartz in the soil aggregates excludes them from being fragments of the weathered crust, while the intimate mixture of organic matter suggests that they are not formed by the cementation of raw glacial drift. The granules may have been the fluffy soil crumbs that develop under bracken or certain kinds of woodland, which have become compacted under a different soil régime as would result from a change in the climate. Such a change could have taken place 3,000 years ago at the

start of the sub-Atlantic period when acid moorland replaced the dominant birch woodland of the preceding sub-Boreal period (Fraser, 1943).

The three principal minerals in the basalt are found to alter in the order olivine, labradorite, augite. In the fresh rock olivine is partly replaced by a finely crystalline mineral identified as vermiculite. Its persistence into the weathered crust and lowest soil horizon is the result of its initial occurrence as large grains, and the fact that there are no grains smaller than 0·1 mm. shows that chemical weathering is more rapid than mechanical comminution. Labradorite and augite on the other hand are abundant in the fine sand and silt fractions of all three soil horizons (Fig. 1). The augite's greater resistance to weathering over labradorite is proved by its survival as spongy allotriomorphic crystals from which intergrown laths of labradorite have weathered and are represented by a kaolin. However, the smallest fragments of labradorite (3 to 2μ) are smaller than those of augite (5 to 3μ) apparently indicating that labradorite is the more stable; possible reasons for this anomaly are that labradorite, having a more pronounced cleavage than augite, is more readily broken down into small fragments, and the slightly stronger diffraction lines of labradorite make it easier to detect in small quantities by X-ray methods.

Jackson, Tyler *et al.* (1948) found that the weathering stage reached in any soil horizon is more advanced with increasing proximity to the surface. Where a profile results from a single set of causes acting upon a uniform bedrock the weathering is accumulative leaving the surface material the most weathered. However, in the Craigpark profile the relationship between bed-rock and soil is complicated by several factors; one is the effect of podzolization under the present or a former climate resulting in translocation of clay and free sesquioxides, while the distribution of quartz shows that the profile has not developed from a uniform bed of basalt, but from a shallow regolith of glacial or periglacial drift. A further complication is the possibility that soil creep has taken place on the 20° slope, the effect of which would be to disarrange the soil horizons. Consequently no conclusion has been reached as to whether weathering is further advanced at the surface or at some depth in the profile. The conflicting evidence has been extracted from Fig. 1 and is listed below.

Alteration greatest at the surface

1. Grains of olivine, the least stable mineral, are found in the lowest horizon only.
2. The ratio augite : labradorite rises from 0·78 below 18 in. to 1·75 in the 3- to 5-in. horizon.

Alteration greatest at depth

1. Abundant grains of basalt are found in the surface horizon, none occur in the 9- to 11-in. horizon.
2. The proportions of free sesquioxides and clay minerals increase with depth.
3. The proportion of quartz increases with depth.

The two clay minerals characteristic of the soil, vermiculite and kaolin, were also found in small quantities in the apparently fresh rock, where their presence may be due to deuteric alteration or to an early stage in subaerial weathering. It was found that vermiculite is produced by the alteration of olivine while the kaolin is secondary to labradorite, thus supporting the contention that the kinds of clay present in soil depend to a great extent on the minerals of the parent rock (Fieldes and Swindale, 1954; Mitchell, 1955). Ross (1943) records montmorillonite from the weathering products of diabase in the eastern United States, which he considers results when ferrous iron, magnesium, alumina, and silica are released as felspar and ferromagnesian minerals decompose simultaneously. However, Walker (1949) considered that montmorillonite results where there is a permanent or fluctuating water table, and that vermiculite is found under conditions of free drainage. The initial presence of vermiculite may also to some extent control the reaction between ions released during weathering and their subsequent crystallization as clay (Van Schuylenborg and Sanger, 1950). Alternatively the clay may be entirely of deuteric origin, its greater abundance in the soil being due to its concentration as other minerals are removed in solution. No other clay minerals were detected with the possible exception of some illite in the weathered crust.

Conclusions

The basalt studied is composed of three principal minerals, olivine, labradorite, and augite, which weather in the order listed. Alteration has commenced in the apparently fresh rock, olivine having given rise to vermiculite and labradorite to a kaolin. The same secondary minerals in greater quantities comprise the clay fraction of the soil, but it was not discovered whether further clay is formed pedologically, or the products of deuteric alteration become concentrated when primary minerals are removed in solution.

Quartz is present throughout the soil profile and it is considered to be glacial contamination. The profile has therefore developed from a mantle of glacial drift of a dominantly basaltic composition, instead of directly from the basalt. During post-glacial time a variety of climates has affected the soil régime, and it is believed that such fluctuations have caused the transformation of a crumb structure into stony granules cemented by free iron oxides and organic matter. The presence of these aggregates in the soil is beneficial in providing a high cation exchange capacity while retaining the working properties characteristic of light soil textures.

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NUMBERS OF BACTERIA AND ACTINOMYCETES IN A KENYA SOIL

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Summary

The estimates of numbers of bacteria and actinomycetes derived from plate counts made from soil samples taken at Muguga, Kenya, varied with the extent to which the soil was diluted. Low dilutions gave small, and high dilutions large, estimates.

The ratio between direct counts and plate counts on the same sample was wide at first, but became narrow as the drought of early 1953 was prolonged.

The percentage of actinomycete colonies on plates was less than 30 at first, but rose to over 90 when the drought was well established.

It is concluded that the drought-resistant part of the microflora in this surface soil is almost entirely composed of actinomycete spores.

A SERIES of counts of the numbers of fungi, actinomycetes, and bacteria in the surface soil of four sites on the farm at Muguga, Kenya, belonging to the East African Agriculture and Forestry Research Organization, was made between November 1952 and May 1953. Some of the results have already been published (Meiklejohn, 1955); but a re-examination of the counts of bacteria and actinomycetes revealed some more points of interest, which are described in this paper.

Material and Methods

The Muguga farm is about 6,800 ft. above sea-level, and the soil is nearly neutral in reaction, heavy, and with a high iron content.

Site A was an arable field which carried wheat in 1952, and was planted with potatoes early in 1953. Sites B and D had been cleared from a wood of Black Wattle (*Acacia decurrens*) and site C was a field of rough grass, formerly under African cultivation. These three sites were burnt over after the first samples were taken (Meiklejohn, 1955).

Samples were taken from the top inch of soil. 10 g. of freshly collected soil were shaken for 3 minutes, by hand, in 100 ml. sterile 0·75 per cent. NaCl for plate counts. Dilutions were made in the same saline solution. Thornton's mannitol-asparagine agar (Thornton, 1922) was generally used for plates, but soil-extract agar (Taylor, 1951), and an agar made with 'Artificial soil solution' (Erikson, 1947) were also used. Four plates were poured from each dilution, and incubated at 30° C. for 7 days.

Direct counts were made by the method of Jones and Mollison (1948); the amount of soil used in this method is determined by the microscope used to examine the slides. In this case 0·2 g. soil in a total volume of 25 ml. was used for each count.

Moisture contents of the samples were estimated by drying them at 105°. The numbers of micro-organisms are given as millions per gram of soil, usually calculated on a dry-weight basis.

Results

Effect of dilution on the plate count

Very early in the work a most disconcerting effect of dilution became apparent; the more dilute the suspension from which a plate count was prepared, the higher the estimate of numbers obtained from the plates. (That is, there were either too few colonies on the plates made from a dilution of 1 in 100,000, or too many colonies on plates made, from the same sample, from a dilution of 1 in 10 million; and it was impossible to tell which of the counts, if any, had any real meaning.) An example is given in Table 1, from which it will be seen that the effect appeared on all three media, and applied to both actinomycetes and bacteria.

TABLE 1

Effect of Dilution on Estimate of Numbers

Sample A3: 4 December 1952

Medium	*Dilution*	*Colonies per plate (mean of 4 plates)*	*Estimated Numbers (millions/g. fresh soil)*
Actinomycetes			
Erikson's agar	$1/10^5$	18·5	1·85
	$1/10^6$	18·5	18·5
	$1/10^7$	7	70
Soil extract agar (Taylor)	$1/10^5$	24	2·4
	$1/10^6$	6	6
	$1/10^7$	3·5	35
Thornton's agar	$1/10^5$	46	4·6
	$1/10^6$	6·5	6·5
	$1/10^7$	3	30
Bacteria			
Erikson's agar	$1/10^5$	40	4
	$1/10^6$	30	30
	$1/10^7$	54	540
Soil extract agar (Taylor)	$1/10^5$	47·5	4·75
	$1/10^6$	19·5	19·5
	$1/10^7$	14·5	145
Thornton's agar	$1/10^5$	203	20·3
	$1/10^6$	37·5	37·5
	$1/10^7$	37	370

The same effect was found throughout the series of counts, as is shown in Table 2, which gives all the counts on Thornton's agar in those experiments where two dilutions were used. As it was obvious that plate counts on these soil samples had no absolute value, the counts made from a dilution of 1 in a million were used for comparative purposes, and Thornton's agar was chosen as a standard medium because it is the easiest of the three to make.

TABLE 2

Effect of Dilution on Counts on Thornton's Agar

Sample	*Actinomycetes* (*millions/g. dry soil*)		*Bacteria* (*millions/g. dry soil*)	
	Estimate from dilution of $1/10^5$	*Estimate from dilution of* $1/10^6$	*Estimate from dilution of* $1/10^5$	*Estimate from dilution of* $1/10^6$
A4	1·9	8·9	17·2	36·2
B3	0·9	10·3	3·4	35·8
B4	1·1	26	3·6	19·7
B5	1·4	12·5	3·4	27·4
C1	7·3	520	16·1	43
C2	33·9	235·4	3·1	33·5
D1	18·8	392	1·7	13·9
D2	29·4	183	1·9	5·1
C5	23·4	237	2·4	4·8
D3	48·5	292	1·6	6·5
A6	33·5	183	5·1	15·5
D4	34·8	260	11	24

The direct count: plate count ratio

All the figures for direct and plate counts are given in Table 3. It will be seen that the numbers recorded in the direct counts are of the same order, some thousands of million cells per gram of soil, as those obtained at Rothamsted by the same method (Skinner, Jones, and Mollison, 1952). There are not enough observations to make it possible to say if there were significant differences between different sites in either direct or plate counts.

The total plate counts are rather high, and the values of the ratio obtained by dividing the direct count number by the plate count number (D/P) are accordingly rather small. The values are given in chronological order in Table 4. In the early counts the D/P ratio was wide, ranging from 39 to 81. Then follows a run of very narrow values, interrupted only by two samples (B7 and C4) which were slightly moister than those before and after them. In sample C5, in fact, the D/P ratio is only 4; that is, the plate count from a dilution of 1 in a million is 25 per cent. of the direct count. At the end of the experiment the D/P ratio was narrower in the samples from burnt than in those from unburnt soils. But no significant relation could be found between the D/P ratio and moisture content.

The numbers of actinomycetes in the plate count

Actinomycete colonies were distinguished from bacterial colonies by examining the plates with a lens. In the early samples they were fewer than the bacterial colonies, making up less than a third of the total plate count. But in all the counts done from 10 February onwards the actinomycetes outnumbered the bacteria, rising to 98 per cent. of the count on two occasions. This high percentage of actinomycetes does not seem to be a specific effect of burning-over the soil; for, as Table 4 shows, the

burnt samples B3, B4, and B5 have low actinomycete percentages, whereas samples C1, D1, A6, and the three unburnt samples taken in May, all have high percentages.

TABLE 3

A Comparison of Direct (Jones–Mollison) and Plate Counts (millions per gram)

Sample	*D Direct count*	*P Total plate count*	*Actinomycetes (plate count)*	*Bacteria (plate count)*
A2	3,448	65·8	7·5	58·3
(A3)	(2,760)	(44·0)	(6·5)	(37·5)
A4	3,634	45·1	8·9	36·2
A6	2,868	198·5	183·0	15·5
Mean	3,317±188	103·1±39·2	66·5±47·6	36·6±10·1
B3	1,808	46·1	10·3	35·8
B4	2,658	45·7	26·0	19·7
B5	2,738	39·9	12·5	27·4
B6	2,311	572·0	525·0	47·0
B7	2,115	42·4	31·2	11·2
B8	1,642	204·3	155·6	48·7
B9	2,607	137·1	92·6	44·5
Mean	2,268±151	155·4±68	121·9±64·9	33·5±5·1
C1	3,123	563·6	520·4	43·2
C2	1,946	268·9	235·4	33·5
C3	2,215	282·0	256·9	25·1
C4	2,297	88·8	72·8	16·0
C5	1,074	241·6	236·8	4·8
C6	1,200	77·1	39·1	38·0
C7	1,856	43·8	31·6	12·2
Mean	1,959±243	222·3±62·8	199±60·4	24·7±15·8
D1	2,821	406·0	392·1	13·9
D2	1,974	188·6	183·5	5·1
D3	1,983	298·5	292·0	6·5
D4	2,865	283·4	259·5	23·9
D5	1,355	152·8	131·1	21·7
D6	2,460	45·7	35·4	10·3
Mean	2,243±217	229·2±47·2	215·6±47	13·6±2·9

Counts made on freshly-collected soil, but calculated as millions per gram of dry soil, except for sample A3 (excluded from the mean). Plate counts from a dilution of one in a million in saline, except for sample A2 (1 in 500,000). 4 replicate plates in every count.

The high percentages of actinomycetes in the plate count seem to be connected with the severe drought of the first three months of 1953. In Fig. 1 the rainfall for periods of five days, from 1 November 1952 to 30 May 1953, is shown with the actinomycete percentages. The effects of drying and wetting the soil seem to take time to appear, as the highest percentages were not found till the drought was well established (see samples B4 and B5), and the high actinomycete counts persisted after the drought had broken; the very wet sample D4 (taken after a night of heavy rain) had 92 per cent. of actinomycete colonies in the plate count.

TABLE 4

Percentage Actinomycetes in Plate Counts, and Direct Count/Plate Count Ratios (in chronological order)

Sample	*Date*	*Moisture content* %	*Per cent. Actinomycetes in plate count*	*D/P*
*A2	25/11	13·0	11	52
*A3	4/12	..	17	63
*A4	13/1	15·8	20	81
B3	23/1	12·6	22	39
B4	27/1	3·7	57	58
B5	4/2	4·3	31	69
*C1	10/2	9·7	92	6
C2	12/2	7·5	88	7
B6	19/2	4·8	92	4
C3	20/2	5·2	91	8
B7	24/2	11·1	74	50
C4	4/3	13·8	82	26
*D1	12/3	6·4	97	7
D2	13/3	6·8	97	10
C5	17/3	6·9	98	4
D3	20/3	4·2	98	7
*A6	9/4	19·1	92	14
D4	15/4	28·8	92	10
B8	13/5	12·3	76	8
*B9	13/5	17·9	68	19
D5	15/5	21·8	86	9
*D6	15/5	24·4	77	54
C6	21/5	6·7	51	16
*C7	21/5	13·8	72	42

* Soil not burned over.

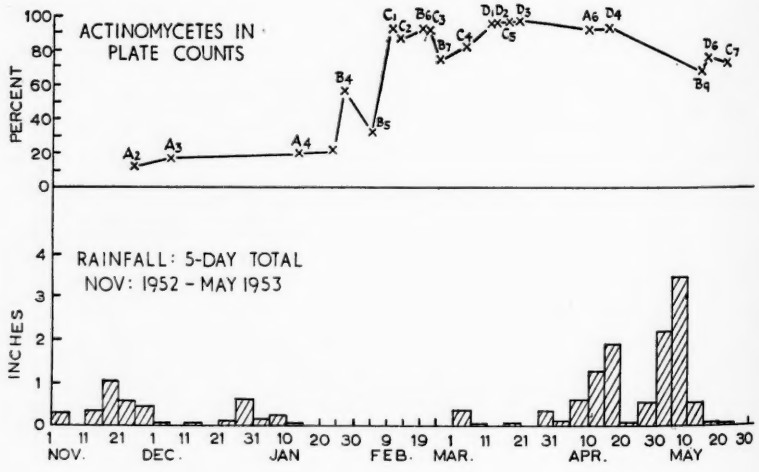

FIG. 1.

No relation was found between the moisture contents and the percentages of actinomycetes, or the numbers of actinomycete colonies. The actinomycetes were probably present in the soil mainly, if not entirely, in the form of spores, as the plate count did not rise with prolonged shaking of the soil suspension, as it should have done had the actinomycetes been in the mycelial stage (Skinner, 1951). Two parallel samples from Site B were shaken for 3 minutes, and for 15 minutes, in saline; shaking for 3 minutes gave an average of 28 actinomycete colonies per plate, and shaking for 15 minutes an average of 26 actinomycete colonies.

As might be inferred from Table 4, the D/P ratios are inversely related to the numbers of actinomycetes in the plate counts. The relationship is an exponential one; the logarithms of the two quantities, plotted against each other, fall on a straight line, which can be expressed by the equation:

$$y = 2{\cdot}0457 - 0{\cdot}6687\,x,$$

where x = log. Actinomycete Numbers (millions per gram soil),

and y = log. Ratio Direct Count:Total Plate Count.

Discussion

The effect of dilution on the plate counts in this work was such that it is quite evident that counts on this soil by the plate method have only a limited and strictly comparative value. If a high dilution was used, a very high plate count was obtained; but if low dilutions had been used throughout this work, a very low estimate of the numbers of micro-organisms would have resulted. It must be noted, however, that preliminary work, in which an attempt was made to plate on Erikson's agar from a dilution of 1 in 20,000, failed because the plates contained so many colonies as to be uncountable. (This very low dilution was tried because Corbet (1934) had found very small numbers of micro-organisms, about 500,000 per gram, in some Malayan soils; he assumed that all tropical soils contain the same small numbers, a conclusion which is evidently wrong.)

This effect of dilution on plate counts does not seem to have been observed by most workers; but Lavergne (1954) reports a similar effect in four counts made apparently on forest soils. Ashworth,* however, observed exactly the same effect of dilution in plate counts made elsewhere in Africa with a non-selective medium. The cause of it might be competition between the developing colonies; but the effect appears in numbers of both actinomycetes and bacteria (see Tables 1 and 2), and on plates which were not visibly overcrowded with colonies. Another possible cause is the presence of some substance in the soil which hindered the development of colonies on agar (cf. Millbank, 1956), this toxic substance being progressively removed by increasing dilution of the soil suspensions.

The ratios between the direct counts and the corresponding plate

* Private communication.

counts (D/P) were, in most cases, narrower than those found by other workers. Skinner *et al.* (1952) found ratios of 40 to 50 in their counts on Broadbalk field at Rothamsted; Thornton and Gray (1950), who used a different direct-count method, found ratios of over 100 in arable, and over 1,000 in some grassland, soils. As the drought of early 1953 progressed at Muguga, the D/P ratio narrowed; that is, a greater proportion of the survivors of the drought were able to develop on the agar plates. There is little doubt that this drought-resistant part of the microflora consists mainly of actinomycete spores. As the relation between the D/P ratio and the actinomycete numbers was exponential, it appears that actinomycetes both survived the drought more easily than other forms; and, having survived, were better able than the other survivors to develop on agar plates. A similar rise in the number of actinomycetes in plate counts during dry weather has been observed in England (Eggleton, 1934), but there it was much less marked than in the Muguga soils. Of course these are an extreme case, as samples taken from the surface in a dry year in a tropical climate must necessarily be. But Laudelout, d'Hoore, and Fripiat (1949) found that forest soils from the Congo gave more actinomycete than bacterial colonies on albuminate agar plates. It is quite possible that actinomycetes, being drought-resistant, make up a large part of the microflora of other tropical soils.

Acknowledgements

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FACTORS AFFECTING THE ABILITY OF PLANTS TO ABSORB PHOSPHATE FROM SOILS

I. THE RELATIONSHIP BETWEEN LABILE PHOSPHATE AND ABSORPTION

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Summary

The relationship between the absorption of phosphate by plants and labile soil phosphate has been investigated in four soils ranging from a calcareous alluvium to basaltic soils of reputed high 'phosphate-fixing' capacity. Labile phosphate has been determined both by isotopic exchange and by applying the principles of isotopic dilution to the results obtained when plants are grown in soils to which labile phosphate has been added (the method of Larsen). The two measures gave generally similar but not identical results.

Aliquots of each soil type were enriched with varying quantities of phosphate to give series of soils similar in all respects other than their phosphate status. The soils were sometimes stored for periods of up to a year before further examination was carried out. A large fraction of the added phosphate always remained in a labile form. In each such series of artificially enriched soils a closely linear relationship was found between absorption by test plants and the labile soil phosphate. Soils of contrasting origin, however, showed no such correlation, but absorption was related to the reciprocal of the quantity of phosphate sorbed by the soils from phosphate solutions under standard conditions.

An interpretation of the factors which determine the extent to which phosphate can be absorbed by plants from different soils is advanced in terms of the concepts of phosphate 'potential' and 'capacity' introduced by Schofield. The labile soil phosphate is not, however, regarded as homogeneous; evidence of wide variation in activation energy between different labile-phosphate fractions has been obtained.

When used to assess the phosphate status of agricultural soils, tracer methods appear to be subject to limitations similar to those of the older extraction procedures.

Introduction

TRACER techniques which depend on the measurement of isotopic exchange or isotopic dilution facilitate the examination of labile phosphate fractions in soil. The extent of isotopic exchange of phosphate between soils and labelled phosphate solutions in which they are suspended (the '*E*' value) has been studied by a number of investigators (McAuliffe *et al.*, 1948; Wiklander, 1950; Russell *et al.*, 1954). A more widely employed tracer procedure was originated by Larsen (1952) who estimated the quantity of soil phosphate with which added labelled phosphate is effectively diluted on its absorption by plants. This quantity, which will be referred to as the 'Larsen' or '*L*' value, has been regarded by Fried and Dean (1952) as a measure of plant-available soil phosphate.

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They therefore adopted the term '*A*' value. The published evidence in support of this interpretation is, however, inconclusive since it has been obtained almost entirely from studies of relatively similar soils which could have been compared with reasonable success by any one of a number of empirical extraction procedures. A more rigorous test of the significance of this measurement would be provided by the investigation of 'phosphate-fixing' soils which cannot be satisfactorily compared by the standard chemical methods. Fried and Dean expressed the opinion that phosphate fixation does not appear to invalidate the *A*-value calculation though they note that restrictions in interpretation may be imposed. On theoretical grounds Russell *et al.*, however, suggested that the method would be inapplicable under such conditions.

In the present investigation three soils with a high capacity for 'fixing' phosphate have been compared with a calcareous soil for the dual purposes of assessing the significance of tracer measurements of labile phosphate and of examining the causes of the apparent low availability of added phosphate in 'phosphate-fixing' soils. It was realized, however, that no complete interpretation of the factors which affect the absorption of phosphate by plants could be reached by examining the equilibria in which phosphate takes part in soil. Nutrient absorption is an active metabolic process and plant physiological factors cannot be ignored. Parallel investigations were therefore devoted to this aspect of the subject. They will be reported separately.

Experimental Methods

The soils used. Details of the soils used are given in Table 1. Extraction with citric acid indicated no marked differences in phosphate status, but the soils contrasted sharply when the absorption of test plants was

TABLE 1

Characteristics of Soils Investigated

Soil	I *Calcareous alluvium*	II *Medium-heavy loam derived from silurian and old red sandstone*	III *Loam basaltic*	IV *Loam basaltic*
Origin	Thames Valley	Edinburgh	Greenhall, Aberdeen	Northern Ireland
pH*	7·6	6·0	5·8	5·5
'Plant available' phosphate: extracted in 1% citric acid (mg. P/5 g. soil) . .	0·56	0·93	0·89	0·64
Absorption by barley under exhaustion conditions (values relative to soil) .	1	0·8	0·2	< 0·01

* pH determined by method of Wright *et al.* (1949).

examined. Whereas barley plants grown in soil I showed no signs of phosphate deficiency, no significant absorption occurred from soil IV in periods of up to 8 weeks unless phosphate was added.

The soils were used both in their natural state and after enrichment with phosphate to varying levels. From each 'parent' soil a series of soils which differed only in their phosphate status was thus obtained. Before use the parent soils were passed through a 2-mm. sieve and mixed in an end-over-end shaker at 20 r.p.m. The orthophosphate necessary to raise the phosphate content of the soils to the desired level was added to air-dry soil in sufficient volume of solution to raise its water content to 6 per cent.—an empirically determined measure of the optimal water content for adequate mixing. The enriched soils were mixed for two periods totalling 2 hours with an intervening period of sieving. They were then air-dried. A comparison of the values of exchangeable soil phosphate in replicate 5-g. samples showed that adequate uniformity was obtained.

Plant-culture methods. Waxed papier-mâché pots of capacity 250 or 500 ml. were used. So that conditions for plant growth would be comparable in all soils a standard weight of washed sand was mixed with the soil for each pot in an electric mixing machine (Kenwood Chef) and nutrients other than phosphate were added. The ^{32}P necessary to determine L values was added during this process. The uniformity of the incorporation of ^{32}P was checked by assaying 5-g. samples under an end-window Geiger-Müller counter. Ten barley seeds (variety Proctor) were planted per pot. After the first leaf had expanded the number of plants was reduced to seven, which gave a close stand at the time of tillering. Watering was carried out by filling glazed earthenware dishes in which the pots were stood. During summer the pots were kept in the open protected from rain by movable 'windolite' screens. In winter a greenhouse was used in which the temperature was kept above 5° C.

Sampling and assay. Roots and shoots were separately assayed. To prevent losses of soluble phosphate from roots during the vigorous washing necessary to separate them from soil the pots were leached with basic lead acetate (Russell and Adams, 1954). Under the conditions of this laboratory the loss of 20 per cent. of the phosphate in roots was thereby avoided.

Calculation of 'L' values. If labelled phosphate is intimately mixed into a soil and plants are grown in it, the amount of soil phosphate, L, with which the labelled phosphate has been apparently diluted on absorption by the plant can be calculated by the equation:

$$L = \frac{Y_f(X_p - D)}{Y_p} - X_f,$$

where X_f and Y_f are the quantities of ^{31}P and ^{32}P added to the soil, X_p and Y_p are the total plant contents of ^{31}P and ^{32}P, and D is the phosphate content of the seed. This procedure is essentially similar to that of Larsen (1952), Fried and Dean (1952), and Gunnarsson and Fredricksson (1953). An allowance for the phosphate content of the seed was not, however, always made by other workers; its omission leads to errors if absorption does not greatly exceed the seed content, since under these circumstances exchange between seed and soil phosphate may affect the specific activity of the plant phosphate to an unknown extent.

The experimental procedure in the present work contrasted with that of previous workers in that the ^{32}P added to the soil was accompanied by a low level of carrier, e.g. 0·01 mg. P/500 g. soil-sand mixture. This had the advantage that the phosphate absorption of the plant as measured by $X_p - D$ was identical with the value obtained in soil before the addition of labelled phosphate. It was found that the magnitude of the L value was not affected by the concentration of carrier even when it was varied by a factor exceeding 1,000; the total quantity of phosphate absorbed by the plants was, however, markedly increased at the high carrier levels (Table 2). Contrary to the recent suggestion of Sokolov

TABLE 2

The effect of the Concentration of Carrier Phosphate on the Absorption by Barley Plants and on Larsen Values

Results expressed as mg. P/5 g. soil.

	Concentration of carrier (mg. P/5 g. soil)			*S.D.*
	0·0002	*0·005*	*1·5*	*($P = 0·05$)*
Soil I Absorption	0·057	0·203	0·349	
	(0·76)	(1·31)	(1·54)	(0·07)
L value	0·46	0·46	0·49	0·06
Soil II Absorption	0·052	0·180	0·180	
	(0·72)	(1·25)	(1·25)	(0·15)
L value	1·00	0·93	0·96	0·07

NOTE. The results for absorption were analysed statistically on a logarithmic basis. Transformed values are shown in brackets.

(1955) this indicates that the lability of soil phosphate was not affected by the addition of phosphate.

Exchangeable soil phosphate E and phosphate sorption S. Aliquots of soil were shaken in labelled phosphate solutions, and the resultant changes in the ^{31}P and ^{32}P content of the solutions were determined. Exchangeable phosphate E and sorbed phosphate S were calculated by the equations:

$$E = \frac{x_t}{y_t} y - x, \qquad S = x - x_t,$$

where x and y are the amounts of ^{31}P and ^{32}P originally present in the solution and x_t and y_t are the corresponding values after equilibration. The reasons for the choice of this method have been discussed by Russell, Rickson, and Adams (1954) who showed that the resultant estimates of E are valid only if the sorbed phosphate remains in isotopic equilibrium with the external solution. If this condition is not satisfied the value of E will change when different quantities of carrier phosphate, x, are used. In all soils the values of E were independent of x and the method was therefore judged to be valid. Typical results are given in Table 3.

The effects of continuous as opposed to intermittent shaking, and of changing the relative amounts of soil to solution, were investigated.

Both variables affected S; E, however, remained relatively constant. To avoid variation in S due to these factors 5 g. soil were treated with 60 ml. solution for each determination and the tubes holding the suspensions were shaken continuously in an end-over-end shaker at 12 r.p.m.

TABLE 3

The Effect of Variation in the Concentration of Phosphate in the Equilibration Solution on Exchangeable Soil Phosphate (E) and on the Sorption of Phosphate (S) in Soil I, Enriched with 1·5 mg. P/5 g. soil

Results expressed as mg. P/5 g. soil.

	Phosphate content of equilibration solution mg. P	*Duration of equilibration (days)*			*S.D.* ($P = 0{\cdot}05$)
		7	*14*	*21*	
Exchangeable soil phosphate	3	1·84	1·89	2·06	0·15
	9	1·89	1·88	2·12	
Sorption of phosphate	3	0·57	0·82	1·00	0·08
	9	1·15	1·66	2·01	

Volume of equilibration solution 60 ml.
Weight of soil . . . 5 g.

The magnitude of E is a function of the time of equilibration. An initial rapid exchange reaction is followed by a slower process which may take many weeks to reach equilibrium (McAuliffe *et al.*, 1948; Russell *et al.*, 1954). For the present purposes little interest attaches to the detailed examination of the change of E with time, and, moreover, analytical considerations would have made such work prohibitively laborious. Accordingly the E values were measured after 7 days' equilibration by which time the rapid exchange reaction was complete and the values were changing relatively slowly. Differences between soils and differences induced in soils by the addition of phosphate, however, affected the extent to which equilibrium was attained in 7 days. For example, the E value for soil IV to which no phosphate had been added increased by 3 per cent. between 7 and 14 days. The corresponding value for soil I to which phosphate had not been added was 19 per cent.; the values for other soils fell between these limits. No values of E obtained in a single equilibration period can therefore be regarded as a precise parameter of the exchangeable phosphate in a soil.

Table 3 shows that the magnitude of sorption, S, varies greatly with the concentration of the equilibration solution. Moreover it is markedly affected by the duration of equilibration, the method of shaking, and by the volume of solution per unit weight of soil. S values can therefore be compared only when the soils under investigation are subjected to

TABLE 4

Plans of Experiments

Expt. no.	*Soil*	*Levels of phosphate enrichment (T) mg. P/5 g. soil*	*Duration of storage (days)*	*Determination of E concn. of ^{31}P in equilibration solution: mg./60 ml. solution*	*Determination of L value and plant intake (P)*			*Date commenced*
					Test crop	*No. of replicates*	*Duration of growth period (days)*	
1	I	0·0, 0·1 0·5, 2·0	nil	1·5	Barley	5	47	26.8.53
2	I	0·0, 0·1 0·5, 2·0	360	1·5	Barley	5	70	23.8.54
3	II	0·0, 0·5 2·0	23	3·0	Barley	3	43	11.12.53
4	II	0·0, 0·5 2·0	75	3·0	..	*E* and *S* are alone determined		
5	III	0·0, 0·5, 3·0 10	15	6·0	..	*E* and *S* are alone determined		
6	IV	0·0, 1·5, 2·8 6·0, 9·0	nil	18·0	Cabbage	5	70	25.9.54
7	I, III, IV	0·0, 1·5	nil	9·0	Barley	5	28, 56, 77	2.5.54
8	I, II, III	0·0, 0·75, 1·5 0·0, 1·5, 3·0	118	9·0	Rye	5	65	25.10.54

NOTE. Three replicates were used in all determinations of *E*. In Experiment 1, *E* was determined after an equilibration period of 4 days; in all other experiments a 7-day period was used.

TABLE 5

Linear Regressions of Plant Absorption (P) on Soil Treatment (T), and on Labile Phosphate Measured as E and L Values

Results expressed as mg./5 g. soil.

Expt. no.	*Test plant*	*Soil*	*Duration of storage (days)*	*P v. T*	*P v. E*	*P v. L*
1	Barley	I	nil	$(0{\cdot}188\pm0{\cdot}008)T+0{\cdot}036$	$(0{\cdot}174\pm0{\cdot}011)E+0{\cdot}001$	$(0{\cdot}205\pm0{\cdot}009)L-0{\cdot}078$
2	Barley	I	360 *F*	$(0{\cdot}156\pm0{\cdot}023)T+0{\cdot}090$	$(0{\cdot}238\pm0{\cdot}022)E-0{\cdot}045$	$(0{\cdot}182\pm0{\cdot}015)L-0{\cdot}021$
			360 *D*	$(0{\cdot}189\pm0{\cdot}021)T+0{\cdot}070$		
3	Barley	II	23 F	.. .. ..	$(0{\cdot}074\pm0{\cdot}009)E-0{\cdot}034$	$(0{\cdot}068\pm0{\cdot}009)L-0{\cdot}012$
			23 D	$(0{\cdot}054\pm0{\cdot}007)T+0{\cdot}015$		
6	Cabbage	IV	nil	$(0{\cdot}025\pm0{\cdot}003)T-0{\cdot}012$	$(0{\cdot}038\pm0{\cdot}004)E-0{\cdot}086$	$(0{\cdot}027\pm0{\cdot}003)L-0{\cdot}032$

NOTES. In the column headed 'Duration of storage' the letters F and D indicate that soils were stored at field capacity or air-dry respectively. Since conditions of storage affect the relationship P v. T separate regressions were calculated for the two storage conditions.

Storage conditions, however, did not affect the relationships P v. E and P v. L. Regressions have therefore been calculated on the pooled data for both storage conditions.

No regression could be calculated for P v. T in the F treatments of Expt. 3 since the small absorption of plants made the data inadequate.

identical treatments. Even then comparisons are qualitative rather than quantitative because the S values for strongly sorbing soils will increase proportionately more than those for weakly sorbing soils when the external concentration is increased. Such comparisons, however, place soils in the correct order with respect to sorption and it is for this purpose only that they have been used in the present study.

Experimental Results

In the first experiments aliquots of individual parent soils were compared after enrichment with different quantities of phosphate. In subsequent experiments aliquots of three parent soils were simultaneously used. The plans of the experiments are summarized in Table 4. As the primary object of the work was to ascertain whether any consistent relationship existed between labile phosphate as measured by E and L and the absorption of plants, wide variations in other conditions were employed; enriched soils were stored before use for periods ranging from nil to 360 days either at field capacity or air-dry; the periods of plant growth ranged from 28 to 77 days; experiments were carried out at different times of year when growth-rates varied greatly, and three test plants, barley, cabbage, and rye, were used.

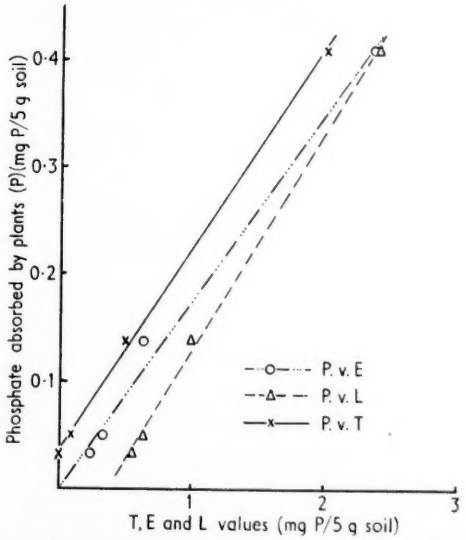

FIG. 1. The relationship between the absorption of phosphate by barley plants (P) in 47 days, the amount of phosphate added to the soil (T), isotopically exchangeable phosphate (E) and the Larsen value (L) in soil I examined immediately after enrichment with phosphate (Expt. 1).

Regression equations:

$$P = (0{\cdot}174 \pm 0{\cdot}011)E + 0{\cdot}001$$
$$P = (0{\cdot}205 \pm 0{\cdot}009)L - 0{\cdot}078$$
$$P = (0{\cdot}188 \pm 0{\cdot}008)T + 0{\cdot}036.$$

1. *Relationship between absorption by plants and labile soil phosphate:*

(*a*) *Experiments with single parent soils.* Statistically significant linear relationships (Table 5) were found between absorption by plants, *P*, and the *E* and *L* values for soils I, II, and IV (soil III was excluded at this stage of the work). In addition absorption was linearly related to the amount of phosphate, *T*, with which the soils had been enriched.

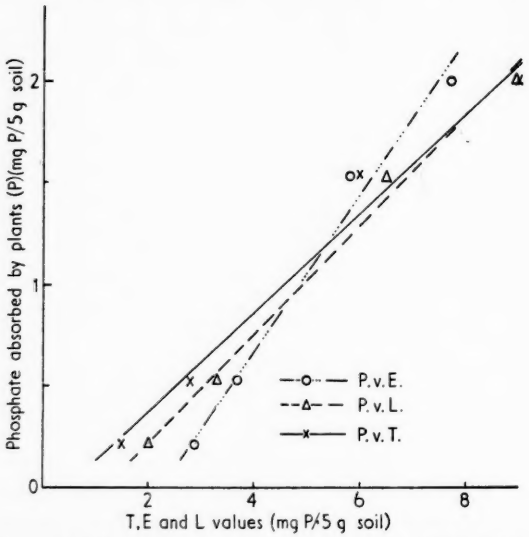

FIG. 2. The relationship between the absorption of phosphate by cabbage plants (*P*) in 43 days, the amount of phosphate added to the soil (*T*), isotopically exchangeable phosphate (*E*) and the Larsen value (*L*) in soil IV examined immediately after enrichment with phosphate (Expt. 6).

Regression equations:

$$P = (0{\cdot}038 \pm 0{\cdot}004)E - 0{\cdot}086$$
$$P = (0{\cdot}027 \pm 0{\cdot}003)L - 0{\cdot}032$$
$$P = (0{\cdot}025 \pm 0{\cdot}003)T - 0{\cdot}012.$$

Representative results are illustrated in Figs. 1 and 2. In Experiments 2 and 3 the enriched soils were stored both at field capacity and air-dry before use. As will be shown in a later section both the *E* and the *L* values were affected by the condition of storage. None the less, when the results for plants grown in soil stored in both conditions were pooled the absorption of plants was linearly related to both *E* and *L* (Fig. 3).

The limited number of points on which the regressions are based made it impracticable to determine whether curvilinear relationships would have given a significantly better fit. In several cases a slight convexity in the relationship of *P* to the other variables was apparent. This was to be expected since absorption ceases to be proportional to the external supply when the nutrient supply is sufficiently increased.

(*b*) *Simultaneous comparison of different parent soils.* Despite the simple

relationship between absorption by plants and both the E and the L values in each of the experiments so far described there were wide contrasts in the slope and the intercepts of the regression lines for the different parent soils (Table 5). This suggested that the simple linear relationships between absorption and labile phosphate was unlikely to

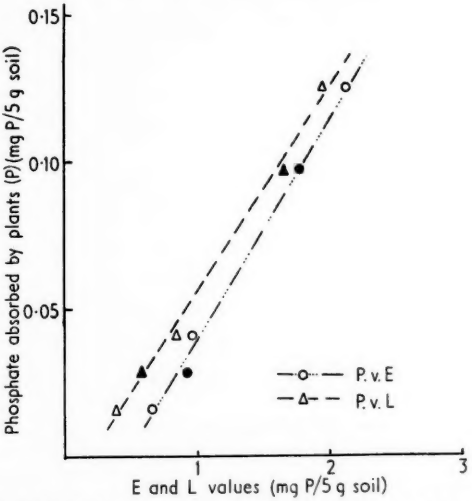

FIG. 3. The relationship between absorption of phosphate by barley plants (P) in 43 days, isotopically exchangeable phosphate (E) and the Larsen value (L) in soil II examined after storage for 23 days at field capacity (closed symbols) and air-dry (open symbols) (Expt. 3).

Regression equations:

$$P = (0{\cdot}074 \pm 0{\cdot}009)E - 0{\cdot}034$$
$$P = (0{\cdot}068 \pm 0{\cdot}009)L - 0{\cdot}012.$$

hold in the comparison of such widely differing soils. Accordingly groups of soils were simultaneously examined.

In Experiment 7 soils I, III, and IV were employed after enrichment with 0·0 and 1·5 mg. P/5 g. soil. Barley was the test plant and three periods of growth, 28, 56, and 77 days, were employed (insufficient supplies of soil caused the final sampling occasion to be excluded with soil IV). The relationship between absorption and labile phosphate is shown in Fig. 4 for the first and second sampling occasions (28 and 56 days). The L values for soils III and IV to which phosphate had not been added are excluded as absorption was too low for unequivocal estimation. In the figure the soils have been arranged from left to right in order of decreasing absorption by the test plants. No general relationship existed between absorption and either measure of labile phosphate but the reciprocal of the value of sorption, S, showed the same general trend as absorption. Comparable results were obtained for the final sampling occasion, there being only small changes in the L value with time (Table 6).

In Experiment 8 soils I, II, and III were used, each enriched to two levels with phosphate (Table 4). The enriched soils had been stored for 118 days both at field capacity and air-dry. Rye, the test plant, was

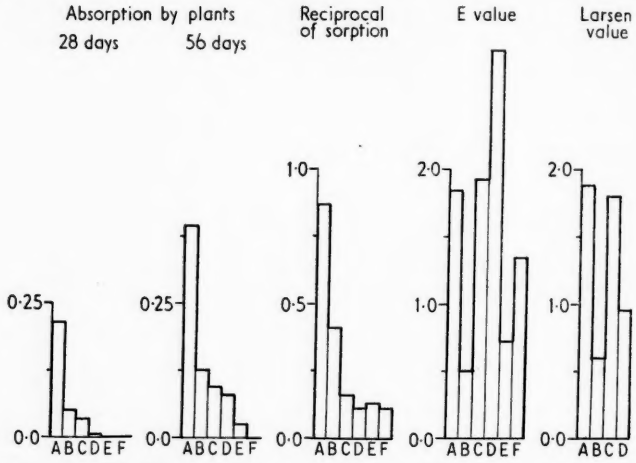

FIG. 4. Absorption by barley plants, isotopically exchangeable phosphate (*E*), the Larsen value (*L*) and the reciprocal of sorption for three soils enriched with phosphate to varying levels immediately before the experiment (Expt. 7).

All values expressed as mg. P/5 g. soil.

Key to Soils:

Soil no.	A I	B I	C III	D IV	E III	F IV
Enrichment with phosphate (mg. P/5 g. soil)	1·5	0	1·5	1·5	0	0

NOTE. Absorption from soils *E* and *F* was too low for the *L* value to be estimated.

grown for 65 days. The results (Fig. 5) are qualitatively similar to those of the previous experiment: the reciprocal of *S* and absorption by plants again varied in the same manner.

In addition to the treatments reported in Fig. 5 soils I and II to which

TABLE 6

Experiment 7: Effect of Duration of Growth of Barley on L Values

Soil no.	*Phosphate added mg. P/5 g. soil*	*L value mg. P/5 g. soil Period of growth (days)*			*S.D.* ($P = 0{\cdot}05$)
		28	*56*	*77*	
I	0·0	0·50	0·59	0·55	0·09
I	1·5	1·82	1·87	1·91	0·09
III	1·5	1·63	1·79	1·72	0·14
IV	1·5	0·94	0·96	..	0·16

no phosphate had been added were used in Experiment 8. They failed to show as close a relationship between the reciprocal of S and absorption as the enriched soils. This can be most conveniently illustrated by comparing the values for these soils with those for the enriched soils

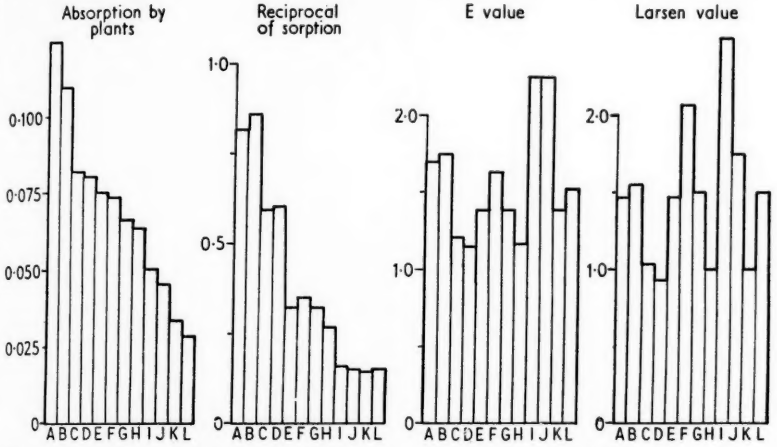

FIG. 5. Absorption by rye plants, isotopically exchangeable phosphate (E), the Larsen value (L) and the reciprocal of sorption for three soils enriched with phosphate to varying levels and stored before use for 118 days at field capacity and air-dry (Expt. 8). All values expressed as mg. P/5 g. soil.

Key to soils:

Soil no.	A I	B I	C I	D I	E II	F II	G II	H II	I III	J III	K III	L III
Enrichment with phosphate (mg. P/5 g. soil)	1·5	1·5	0·75	0·75	1·5	1·5	0·75	0·75	3·0	3·0	1·5	1·5
Condition of storage	F	D	D	F	F	D	D	F	D	F	F	D

F = Field capacity. D = Air-dry.

from which the absorption of plants was of similar magnitude. The following figures enable this comparison to be made for soil I to which no phosphate had been added:

	Absorption by plants (mg. P/5 g. soil)	*Reciprocal of S*
Soil III, 1·5 mg. P/5 g. stored at field capacity	0·032±0·003	0·14±0·005
Soil I, no P added	0·030±0·003	0·42±0·005
Soil III, 1·5 mg. P/5 g. stored dry	0·029±0·004	0·14±0·005

Soil II to which phosphate had not been added showed a smaller though similar discrepancy from the general trend. These observations suggest

that the relationship between P and the reciprocal of S found in the enriched soils cannot be regarded as of universal occurrence.

Relationship between E and L values. The similarity of the relationships between absorption by plants and both the E and L values for series of soils prepared by enrichment of the same parent soils indicates that

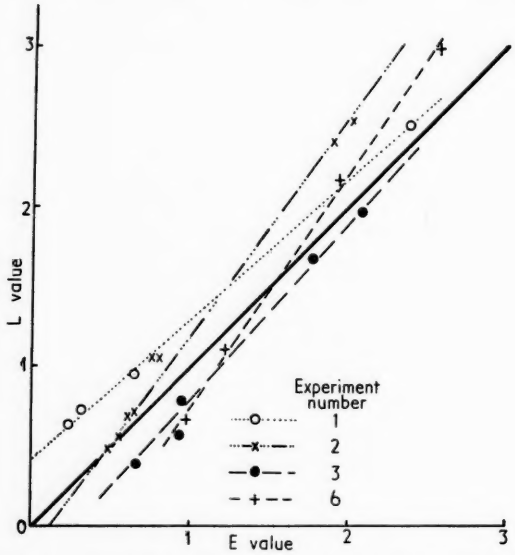

FIG. 6. Relationship between the Larsen value (L) and exchangeable phosphate (E) in soils examined in different experiments.

The heavy line indicates the relationship $L = E$.

Regression equations:

Expt. 1 $L = (0{\cdot}85 \pm 0{\cdot}03)E + 0{\cdot}38$
2 $L = (1{\cdot}32 \pm 0{\cdot}03)E - 0{\cdot}14$
3 $L = (1{\cdot}08 \pm 0{\cdot}14)E - 0{\cdot}31$
6 $L = (1{\cdot}45 \pm 0{\cdot}11)E - 2{\cdot}07$.

both measures of labile phosphate were affected in the same general manner by soil treatments. Qualitative differences were, however, apparent. To examine such relationships linear regressions of L on E were calculated for those experiments in which one parent soil was used at three or more levels of enrichment (Table 7). Representative data are shown in Fig. 6. Highly significant relationships were established and in 3 out of 4 cases the regression coefficients were significantly different from 1. A significant change in the relationship was induced by storage of soil I (compare Expts. 1 and 2, Table 7). In Experiment 8 the relationship between L and E was examined for all soil treatments (i.e. soils I, II, and III enriched to varying levels and stored at field capacity or dry). Once again a highly significant linear relationship obtained (Fig. 7); the regression coefficient was not significantly different from

TABLE 7

Relationship between Quantity of Phosphate added to Soils (T) and Labile Phosphate as Measured by E and L Values

Results expressed as mg. P/5 g. soil

Expt. no.	*Test plant*	*Soil*	*Duration of storage (days)*	*E v. T*	*L v. T*	*L v. E*
1	Barley	I	nil	$(1{\cdot}07\pm0{\cdot}05)T+0{\cdot}20$	$(0{\cdot}92\pm0{\cdot}02)T+0{\cdot}55$	$(0{\cdot}85\pm0{\cdot}03)E+0{\cdot}38$
2	Barley	I	360 F	$(0{\cdot}68\pm0{\cdot}03)T+0{\cdot}55$	$(0{\cdot}90\pm0{\cdot}03)T+0{\cdot}58$	$(1{\cdot}32\pm0{\cdot}03)E-0{\cdot}14$
			360 D	$(0{\cdot}76\pm0{\cdot}05)T+0{\cdot}51$	$(1{\cdot}00\pm0{\cdot}04)T+0{\cdot}52$	
3	Barley	II	23 F	$(0{\cdot}58\pm0{\cdot}05)T+0{\cdot}62$	.. .. ..	$(1{\cdot}08\pm0{\cdot}14)E-0{\cdot}31$
			23 D	$(0{\cdot}74\pm0{\cdot}05)T+0{\cdot}63$	$(0{\cdot}77\pm0{\cdot}13)T+0{\cdot}42$	
4	..	II	75 F	$(0{\cdot}56\pm0{\cdot}04)T+0{\cdot}54$	Not determined	
			75 D	$(0{\cdot}69\pm0{\cdot}05)T+0{\cdot}56$		
5	..	III	15 F	$(0{\cdot}67\pm0{\cdot}01)T+0{\cdot}92$	Not determined	
			15 D	$(0{\cdot}71\pm0{\cdot}02)T+0{\cdot}92$		
6	Cabbage	IV	nil	$(0{\cdot}66\pm0{\cdot}03)T+1{\cdot}79$	$(0{\cdot}93\pm0{\cdot}07)T+0{\cdot}70$	$(1{\cdot}45\pm0{\cdot}11)E-2{\cdot}07$

NOTES. In the column headed 'Duration of storage' the letters F and D indicate that soils were stored at field capacity or air-dry respectively. Since conditions of storage affect the relationships E v. T and L v. T separate regressions were calculated for the two storage conditions.

Storage conditions, however, did not affect the relationship L v. E. Regressions have therefore been calculated on the pooled data for both storage conditions.

No regression could be calculated for L v. T in the F treatments of Expt. 3 since the small absorption of plants made the data inadequate.

unity while the constant in the regression equation was small. An examination of Fig. 7 suggests, however, that storage at field capacity reduced L relative to E to a small extent. E and L may therefore be regarded as alternative measures from the viewpoint of examining the relationship between the labile phosphate in these soils and the absorption

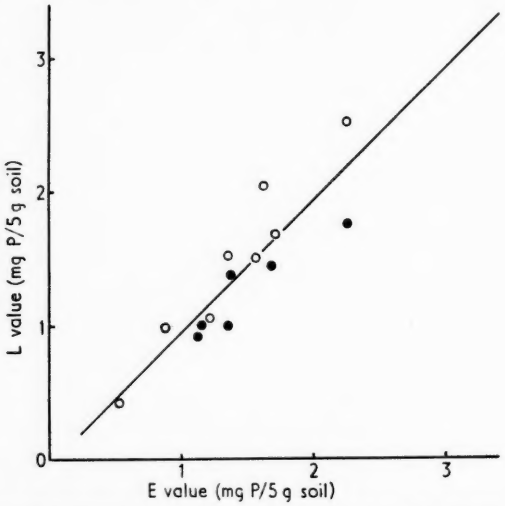

FIG. 7. Relationship between the Larsen value (L) and exchangeable phosphate (E) for soils I, II, and III enriched to different levels with phosphate and used simultaneously after storage at field capacity (closed symbols) and air-dry (open symbols) for 118 days (Expt. 3).

Regression equation: $L = (0{\cdot}99 \pm 0{\cdot}13)E - 0{\cdot}04$.

of test plants. However, as is apparent from Table 7 and Fig. 6, small but significant differences occur between these quantities.

The effect on labile phosphate of the addition of phosphate to soils. In all experiments in which a series of three or more soils were prepared by the enrichment of a single parent material highly significant linear regressions were established between labile phosphate measured as E or L and the amount of phosphate which had been added (Table 7). The coefficients in the regression equations are measures of the increments in E and L induced by unit addition of phosphate (i.e. $\Delta E/T$ and $\Delta L/T$). When too few points were available for regressions to be fitted $\Delta E/T$ and $\Delta L/T$ were calculated, though with less precision, from the increments induced in E and L by treatment with phosphate. The results obtained by both methods are summarized in Table 8, those determined from regressions being indicated by the inclusion of 5 per cent. fiducial limits. Although the experiments were not designed for the detailed examination of these relationships certain conclusions may be drawn.

When the soils were stored $\Delta E/T$ and $\Delta L/T$ fell below 1 except with soil I in which all the added phosphate contributed to the L value after

TABLE 8

Changes in E and L values induced by the Addition of Phosphate (T) to Different Soils—Summary of Results

Soil	*Duration of storage*	*Expt. no.*	$\Delta E/T$	$\Delta L/T$	*Test plant*
I	nil	1	1·07±0·05	0·92±0·02	Barley
	nil	7	0·9	0·9	Barley
	118 F	8	0·8	0·7	Rye
	118 D		0·8	0·8	
	360 F	2	0·68±0·03	0·90±0·03	Barley
	360 D		0·76±0·05	1·00±0·04	
II	23 F	3	0·58±0·05	..	Barley
	23 D		0·74±0·05	0·77±0·13	
	75 F	4	0·56±0·04	..	..
	75 D		0·69±0·05	..	..
	118 F	8	0·4	0·3	Rye
	118 D		0·5	0·7	
III	nil	7	0·8	..	..
	15 F	5	0·67±0·01	..	..
	15 D		0·71±0·02	..	..
	118 F	8	0·5	0·5	Rye
	118 D		0·5	0·5	
IV	nil	6	0·66±0·03	0·93±0·07	Cabbage
	nil	7	1·0	..	..

NOTE. In the column headed 'Duration of storage' the letters F and D indicate that soils were stored at field capacity and air-dry, respectively.

360 days. With the exception of soil II the values ranged from 0·5 upwards; over 50 per cent. of the added phosphate had therefore remained labile. The condition in which the soils were stored had little effect on $\Delta E/T$ or $\Delta L/T$. The very wide differences in the ability of plants to absorb phosphate from the different soils (Figs. 4 and 5) was therefore not dependent on the conversion of added phosphate to non-labile forms.

The effect of the addition of phosphate on the ability of soils to sorb phosphate. The enrichment of soils with phosphate progressively decreased the values of sorption but no quantitative relationship was apparent. The complexity of the mechanism of sorption is indicated by experiments with soils which had been so greatly enriched with phosphate that desorption of phosphate occurred in the early stage of shaking with phosphate solutions. With the passage of time this effect was reversed and in some cases significant sorption eventually occurred. Soil I which had been stored dry for 360 days after enrichment with 2 mg. P/5 g. soil gave the following results when shaken in a solution containing 1·5 mg. P/60 ml.:

Period of equilibration	*Sorption (S)*
2 days	−0·18 mg. P/5 g. soil
7 days	−0·03
14 days	+0·13
	S.D. 0·04

This suggests that the added phosphate can migrate between sites which have different characteristics. This mechanism could explain the contrasting relationships between the absorption of plants and sorption which resulted from the enrichment of soils with phosphate in Experiment 8.

Discussion

In soils of similar origin (i.e. the same parent soils enriched with varying quantities of phosphate) it has been shown that absorption by plants is closely related to labile soil phosphate. No such relationship, however, exists when contrasting soil types are compared. Neither the *E* nor the *L* value can therefore be regarded as a measure of 'plant available' phosphate. Furthermore the occurrence of high *E* and *L* values in soils from which plants were able to absorb only relatively small quantities of phosphate (e.g. soil III, Fig. 5) indicates that the characteristic of phosphate 'fixation' normally ascribed to such soils is not primarily due to the precipitation of phosphate in insoluble forms. This conclusion is supported by the fact that over the longest periods for which observations were made the *E* and *L* values of these soils were increased to an extent which rarely fell below 50 per cent. of the amount of phosphate which had been added to them (Table 7). The characteristic of the 'phosphate fixing' soils which was most closely related to their ability to provide phosphate to plants was the reciprocal of the extent of sorption (Figs. 4 and 5). Although the measurements of sorption here reported are qualitative rather than quantitative, differences in the reciprocals of these values clearly reflect differences in the free energy of phosphate in the soils. The simplest interpretation of the present results therefore appears to be that the basaltic soils contain large numbers of sites which have sufficient affinity for labile phosphate ions to prevent their absorption by plants. Thus the quantity of phosphate which plants can absorb from such soils may be low even though the soil may contain larger quantities of labile phosphate than soils of apparently high phosphate status which have a smaller capacity for sorption (compare soils I and IV, Fig. 4; soils I and III, Fig. 5).

These findings accord with the recent theoretical analysis of Schofield (1955) who has concluded that the term 'available soil phosphate' is not applicable to any discrete phosphate fraction. He has suggested that a more adequate interpretation of the phosphate relations of soils could be achieved by considering two parameters of the labile phosphate of the soils—its 'potential' and its 'capacity'. The terms are used in the thermo-dynamic sense and their product gives the 'quantity' of labile phosphate in the system. A similar approach has greatly aided the study of water relations in the soil. The reciprocal of *S* as measured in the present work is qualitatively related to the 'phosphate potential' while *E* and *L* values provide estimates of the 'quantity' of labile phosphate. This hypothesis implies that the determination of a single parameter can be expected to provide a satisfactory comparison of the ability of soils to provide phosphate to plants only when there is a constant relationship between the 'capacity' and the 'potential' of the soils under

comparison. In the present experiments this condition was satisfied when a series of soils were prepared by the enrichment of a single parent material. Conventional chemical extraction procedures permit valid estimates of the *relative* phosphate status of soils under such conditions. The term *A* value or 'measure of available phosphate' therefore appears as applicable to these procedures as to Larsen's calculation.

Despite the fact that *L* values reflect plant physiological factors in addition to physico-chemical relations in the soil they have been shown to be in general similar to *E* values, and closely linear relations exist between the two quantities when series of similar soils are compared. Significant differences between them had, however, been shown (Table 7). When the *L* values were less than *E* the simplest explanation is that certain phosphate fractions were retained in the soil at a potential which made them inaccessible to plants although they remained readily exchangeable.

The occurrence of *L* values which exceed *E* is considered to be due to labile soil phosphate which contributes to the *L* value not undergoing isotopic exchange in the 7-day period used to determine the *E* values. An alternative explanation of this situation would be that the action of plant roots in absorbing other ions caused non-labile phosphate to be rendered into a labile form. However, had this occurred, the *L* values would have been expected to increase as the growth period of the plants was prolonged and the effect would have been greatest in the most highly enriched soils which permitted the greatest growth and absorption. Neither of these effects was observed and it therefore appears unlikely that plants converted non-labile phosphate into labile forms to a significant extent.

The complexity of the equilibria in which labile soil phosphate takes part has been illustrated by a number of observations. Complete isotopic equilibrium between soils and labelled phosphate solutions in which they are suspended may not be attained for several weeks (Russell *et al.*, 1954); the relative magnitude of the *E* and *L* values may change with time (Table 8) and some observations make it appear probable that labile phosphate can migrate slowly between sites with different characteristics. This is highly suggestive that the labile phosphate in the soil consists of many fractions, differing in activation energy, which could be distinguished by sufficiently precise methods. The very slow migration of phosphate in soils, which has been demonstrated in many tracer investigations, provides further evidence of slow reaction rates. During the course of experiments of the type here reported true equilibrium is never attained. The applicability of the concept of 'phosphate potential' is however in no way invalidated by the inhomogeneity of labile phosphate.

When soils of similar type are compared (i.e. soils prepared by enrichment of the same parent soil in the present experiments) both give equally good correlations with plant absorption (see Figs. 1–3). Hence for the agronomic purpose of comparing the relative phosphate status of soils it may be concluded that the *E* and *L* values are sufficiently similar for them to be regarded as alternative measures. The choice between the two procedures for this purpose should therefore depend mainly on

convenience and economy of labour. On these grounds the E value procedure is greatly to be preferred. It is surprising therefore that the Larsen method has received much greater attention (*vide* Dean, 1955).

In conclusion the implications of the present work with regard to the value of isotopic measurements of labile phosphate in soils may be considered. Their limitations for the assessment of soil fertility have been emphasized, though the possibility merits further examination that the simultaneous determination of E and S values may, when judged in terms of labour expended and information gained, prove an alternative to conventional chemical extraction procedures. The method has potential use also for the comparison of different phosphatic fertilizers which have been added to a single test soil. It is, however, in fundamental investigations rather than in soil testing that the real value of tracer studies of labile phosphate appear to lie. The detailed examination of the relationships between E and L values in different soils can yield information not obtainable in other ways. New information should come from a systematic examination of the effects of the addition of phosphate on the labile phosphate fractions of different soil types subjected to contrasting treatments. Furthermore, as will be shown in a subsequent paper, a comparison of the L values obtained with different plant species may provide evidence on differences in their absorption mechanism.

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CHEMICAL STUDIES ON PODZOLIC ILLUVIAL HORIZONS

I. THE EXTRACTION OF ORGANIC MATTER BY ORGANIC CHELATING AGENTS

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Summary

In qualitative studies with a number of soils, organic reagents such as aqueous acetylacetone or cupferron were found to extract a large fraction of the organic matter from podzolic B horizons; smaller quantities were removed from two humic-gley A horizons. All other soil types tested yielded negligible amounts of carbon with this treatment. Substitution of Cu for the exchangeable cations of a typical Australian black earth followed by treatment with acetylacetone did not result in an increase in organic matter extracted over the untreated soil. It is concluded that, to be extracted by solutions of organic chelate compounds, soil organic matter must be immobilized by ions of one of the transition metals, and the H form must be readily dispersed; it is also possible that large amounts of clay may inhibit extraction. This type of organic matter probably occurs only in the podzolic group of soils.

A comparison of the extractive properties of several reagents on two Queensland ground-water podzols is presented. Cupferron is the most efficient, but complete removal of excess reagent from the final suspension is difficult. Acetylacetone (in water) and oxine (in 50 per cent. acetone) extract a large fraction of the total organic carbon and most of the Al, but the presence of acetone partially inhibits the extraction of carbon. Aqueous oxine is unsatisfactory owing to the extreme dilution of the saturated solution. It is concluded that acetylacetone is the most useful reagent so far tested owing to its miscibility with water and formation of stable ether-soluble complexes with Fe and Al. Attempts to fractionate the B-horizon humus, using salicylaldehyde, acetylacetone and oxine which form progressively more stable complexes with Fe and Al, were unsuccessful owing to the dispersing effect of the NaOH added to adjust the pH values of each reagent. It is suggested that factors controlling the flocculation of organic colloids from soil suspensions are equally as important as the bonding energy of the metal-organic matter bonds in determining the extent of dispersion.

ALONG the coastal belt of south-east Queensland a number of soil profiles occur showing the morphological features of ground-water podzols (Hubble, 1954). These soils are developed on sandy alluvium and are characterized by grey sandy A_1 horizons, followed by compacted, faintly mottled A_2 fragipans overlying weakly cemented dark-coloured organic B horizons. These soils show some similarities to the 'padang' soils of Borneo described by Hardon (1937) and to the lowland tropical podzols discussed by Richards (1941); other common features are the small quantities of iron in the profile (Richards records negative Comber tests on similar soils in British Guiana and Sarawak), low clay content, and high C/N ratio in the B horizon. In chemical studies of the humus layer from the Queensland soils it was found that a number of organic reagents forming ether-soluble metal chelates were able to peptize considerable quantities of organic matter in aqueous or aqueous acetone solutions. As reported in a preliminary note (Martin and Reeve, 1955)

the organic matter from a number of other soil types failed to disperse by this treatment. In view of the possible importance of this phenomenon in connexion with the podzolization process a more intensive study of the amounts of organic matter (and associated metals) extracted was undertaken, the results of which are reported in this paper.

Experimental

Small portions of air-dry soils (< 2 mm.), representing some great soil groups from Australasia and overseas, were placed in contact for some hours with aqueous solutions of cupferron or acetylacetone (0·20–0·07 M) with occasional shaking, and then allowed to stand overnight. Next day the colour of each supernatant liquid was noted. All the acetylacetone series and some of the cupferron extracts were extracted with ether and the colours of both layers were observed after allowing the phases to separate. Qualitative results from some of the soils tested are shown in Table 1. Both reagents released appreciable amounts of dark-coloured material from most podzol B horizons, irrespective of origin. Their effect on other soil types was negligible and, although slightly coloured compounds were extracted from some soils, ether extraction of the suspension caused the transfer of most of the colour to the ether layer. It was assumed that free Fe_2O_3 in the soil had reacted with both reagents, giving ether-soluble coloured complexes. There was some extraction of dark-coloured material from both low humic gley surface horizons; the presence of clay appeared to inhibit the extraction of organic matter. It is of interest, in this connexion, that all the podzol illuvial horizons studied contained only small amounts of clay.

TABLE 1

Extraction of Organic Matter from Different Soil Types

Soil Type		*Horizon*	*Colour of suspension*		*Colour of ether layer*	
			Cupferron	*Acetylacetone*	*Cupferron*	*Acetylacetone*
Ground-water podzol, Tasmania		B	Yellow	Brown	..	Yellow
Ground-water podzol	Queensland	B	Dark brown	Sl. brown	..	Colourless
Rendzina		A	Colourless	Colourless	..	Yellow
Black earth		A	,,	,,	..	,,
Red loam		Surface	Pale yellow	,,	..	,,
Red loam		Subsurface	Colourless	Faint yellow	..	,,
Krasnozem		Surface	Yellow	,,	..	,,
Podzol, Scotland (Glendye 5)		B	Brown	Brown	Orange	Orange
Podzol, New Zealand (Te Kopuru sand)		B	Brown	Dark brown	Colourless	Pale yellow
Low humic gley I (50% clay)	Q'ld.	A	Faint brown	..	..	..
Low humic gley II (2% clay)	Q'ld.	A	Medium brown	..	..	..

Since the translocated organic matter of podzols is generally associated with tervalent metals, and since reagents such as cupferron or acetylacetone complex only weakly or not at all with alkaline earth metals at the normal pH range of soils, it was argued that complex formation with Fe or Al (or both) was a necessary prerequisite for the release of soil organic matter as a dispersed phase. This would explain the lack of release of organic matter by rendzina soils, for example. It was further considered likely that replacement of the Ca and Mg by a metal

forming strong complexes with organic reagents (e.g. Cu) would render the organic fraction readily dispersible in a solution of one of these reagents.

One sample of the surface horizon of a black earth was washed with 0·02 N HCl to remove exchangeable cations and leached with 1,000 ml. 0·05 N $CuSO_4$. After washing the Cu soil free of excess metal with distilled water it was air-dried, ground to pass a 1 mm. sieve, and a weighed portion treated with 0·2 M acetylacetone. Some dark-coloured material was extracted in greater quantity from the Cu-soil than from a similar portion of the original soil that had received no Cu treatment. The results in Table 2, however, show that extractable organic carbon (Walkley and Black, 1934) was slightly decreased by Cu treatment and was, in either case, only a small fraction of the total organic carbon. The increase in colour with Cu treatment may have been caused by reduction of hydrous oxides of Fe or Mn by Cu treatment (an effect noted with higher Mn oxides in organic soils by Heintze and Mann (1949)) and formation of coloured complexes with acetylacetone.

TABLE 2

Effect of Cu *Treatment on Extractability of Carbon, Aluminium and Iron from a Black Earth*

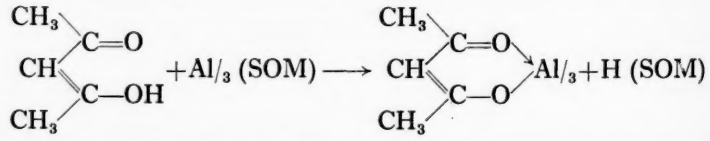
(Results as % air-dry soil)

	Carbon	*Iron*	*Aluminium*
Original soil . .	0·19	0·002	0·12
Cu-treated soil .	0·16	0·005	0·09
Total present . .	1·44	..	..

From these experiments it was postulated that the extraction of organic matter from soil by organic complex-forming compounds is governed by three conditions:

1. The extractable organic fraction must be immobilized in the soil by Fe, Al, or any transition metal which forms strong complexes with the reagents used, within the normal range of soil pH.

2. The organic residue, from which these metals are removed by complexation, must be dispersed to a considerable degree in its hydrogen form, as shown by the following schematic reaction involving acetylacetone and soil organic matter (SOM) immobilized with aluminium:



This argument does not apply to cupferron, which is the ammonium salt of nitrosophenylhydroxylamine and hence would form NH_4-humus by complexation. Condition (1) would, however, be satisfied by this reagent.

This property is further confirmed by the fact that organic matter, free Al^{+++} (and in some cases Fe^{+++} also) are readily removed from all

the podzolic soils listed in Table 1, except that from Tasmania, by treatment with 0·2 N mineral acid. If the acid-treated soils are then washed with water, an increase in humus dispersion occurs in most cases, accompanied by a sharp drop in the release of metal ions.

3. Results on the humic gley soils in Table 1 suggest that the presence of clay inhibits organic matter extraction by these reagents. The nature of the association between translocated humus and some clay minerals, and its effect on extractability with organic reagents, will be the subject of further studies.

Quantitative studies

A brief investigation of the extractive properties of some organic reagents on a quantitative basis was then undertaken, and the results are reported in the following sections.

From the large numbers of organic reagents which can chelate with Fe or Al the choice of compound used was limited as a result of the following considerations:

First, it is desirable that metal complexes formed with the reagent, and also the reagents themselves, are soluble in solvents immiscible with water, permitting their complete extraction from the suspension. This property is not possessed by water-soluble chelating compounds such as citrate, pyrophosphate, or salts of ethylenediaminetetraacetic acid.

Second, the most satisfactory reagents are water-soluble, since the use of organic solvents (in which many reagents are exclusively soluble) may retard dispersibility. Thus, while acetone is a good solvent for oxine (8-hydroxyquinoline) the dispersion of H-organic matter is greatly reduced in this solvent.

Third, stable complexes should be formed with tervalent metals. Some substituted β-diketones such as acetoacetic ester are not satisfactory from this viewpoint (Martell and Calvin, 1952) in spite of the fact that their immiscibility with water and partition coefficient with ether or chloroform are favourable.

Oxine, since it forms strong complexes with Fe and Al, is theoretically an ideal reagent, but has the disadvantage of low water solubility (0·052 per cent. at room temperature according to Lacroix, 1947). Nevertheless, in view of its importance in analytical chemistry, some extractions were performed with this reagent in aqueous acetone; the effect of acetone concentration on organic matter dispersion was also studied.

Description of soils

Samples from two ground-water podzols from coastal Queensland were employed in this study. Both profiles occur under heath vegetation (*Banksia* spp. with proteaceous plants and sedges) on the so-called 'wallum' country (Coaldrake, 1956—unpublished). The parent material is sandy alluvium, probably derived from Mesozoic sandstones which outcrop in the area. Sample 813 (50–57 in.) is an organic sand pan from a profile near Sippy Creek; sample 820 (38–54 in.) was taken from a similar soil in a more elevated position at Beerwah. Each layer, which is dark brown to black in colour, underlies a compacted siliceous fragipan.

Both profiles are subject to regular seasonal saturation and the water-table is high throughout the summer. Proximate analyses of the air-dry samples (percentage basis) are as follows:

	pH	*Total* C (*Walkley-Black*)	*Total* Al	*Total* Fe	C/Al *ratio*
813	4·8	3·60	0·70	0·06	5·1
820	4·6	2·71	1·39	0·18	1·9

Total Fe is a relatively minor constituent of both soils and Al was therefore assigned a major role in stabilizing the organic matter. In this paper results for extractable Al only are presented and the removal of Fe is discussed more fully in a succeeding publication.

General technique for organic matter extraction

One to 5 g. air-dry soil (< 2 mm.), depending on the content of organic carbon, were extracted with an aqueous or aqueous acetone solution of reagent, which varied in concentration according to need but was generally 0·2 M. No special precautions were taken to purify any reagent; laboratory grade materials always gave satisfactory blank values. The soil-solution ratio was usually 1:25. The suspension was shaken by hand occasionally over some days and then centrifuged to bring down mineral particles (2,000 r.p.m. for 30–60 minutes was usually sufficient). The soil residue was washed repeatedly with water or aqueous acetone until washings were clear and colourless on recentrifuging; a final acetone wash removed last traces of Al or Fe complex entrained in the soil.

The extract and combined washings were transferred to a liquid-liquid extractor of the upward displacement type and extracted overnight with diethyl ether. This method of solvent extraction is preferable to manual extraction with separating funnels owing to the formation of intractable emulsions with the latter method. The receiver then contained an ether solution of metal chelates and excess reagent. After recovery of most of the ether the residue was digested with 1 ml. conc. sulphuric acid at low heat until charring occurred, cooled and re-digested with 3 ml. 72 per cent. perchloric acid until fuming strongly. The clear digest was then cooled and diluted to volume, and aliquots taken for determination of Al (Pellowe and Hardy, 1954) and Fe (*o*-phenanthroline method in presence of citrate as described by Sandell, 1944).

The suspension was freed from organic solvent, usually by heating on a water bath under reduced pressure, and diluted to a convenient volume. Aliquots were taken for organic carbon determination by the method of Walkley and Black (1934). All results were calculated on the air-dry soil basis.

Typical results are given in Table 3 showing the effect of a number of reagents on the Sippy Creek B_2 horizon. For comparison, results of a pyrophosphate extraction are included.

Using the pyrophosphate extraction as a basis for comparison, it is clear that the organic reagents tested are much slower in their effect on

the release of both organic carbon and Al. Cupferron appears considerably more efficient than acetylacetone in the extraction of C, since comparable amounts are extracted by the latter reagent at approximately eight times the concentration of cupferron although the time of extraction favours acetylacetone in one instance.

TABLE 3

Extraction of Organic Carbon and Aluminium from Sippy Creek Soil (no. 813)

Reagent	*Solvent*	*Time of extraction (days)*	*% total constituent extracted*		
			C	Al	C/Al *ratio*
Cupferron 0·013 M	Water	3	51	21	6·4
,, 0·064 M	,,		94	30	8·2
Acetylacetone, 0·1 M	,,	6	45	15	7·6
,, 0·5 M	,,	0·75	94	40	6·2
Oxine, saturated	,,	1·6	4·4	2·9	4·0
,, 0·07 M	50% acetone	7	41	50	4·2
Sodium pyrophosphate 0·2 M (pH 7·0)	Water	(1 hour)	100	43	6·0

Aqueous oxine is clearly quite inefficient owing to the low water solubility of the reagent; in the presence of acetone the more concentrated oxine solution extracts considerable quantities of the total C and Al although this release is the least rapid of the three reagents tested. It is noteworthy that the C/Al ratio of both oxine extracts are appreciably lower than those for all other reagents. The strongest cupferron reagent extracts the most C in relation to Al, and, from the odour of the final suspension, it was suspected that small quantities of free reagent were still present, in spite of repeated ether-extraction of the original suspension.

The effect of acetone concentration

As the previous results indicated that oxine in aqueous acetone possessed distinct possibilities as an extractant, separate 1 g. portions of soil 820 were extracted with 50 ml. portions of 0·1 M reagent (oxine and acetylacetone were used in this experiment) for 4 days. The reagent solutions contained varying proportions of acetone and, after centrifuging, each soil residue was washed with a mixture of acetone and water in the same ratio as that employed in extraction. Table 4 shows the amounts of C and Al removed by these treatments.

Except in pure water where the low solubility of oxine limits extraction of organic carbon, acetylacetone is less efficient than oxine at each level of acetone concentration, while oxine extracts much greater amounts of Al than acetylacetone in relation to the quantity of organic C extracted.

After the final acetone washing, the oxine-treated soils were dried in a current of air and dispersed in pure water with shaking. After some days, further amounts of organic matter were released, the depth of

TABLE 4

Effect of Acetone Concentration on Release of Organic C *from Beerwah Soil (820) after 4 days*

Total organic carbon (Walkley-Black) = 2·71%
Total aluminium . . . = 1·39%

Volume ratio Acetone : water	*Fraction (%) total constituent extracted*			
	0·1 M *Acetylacetone*		0·1 M *Oxine*	
	C	Al	C	Al
0/100	37	5·8	13*	2·2*
20/80	39	3·6	49	18·7
40/60	30	4·3	43	16·5
50/50	..	..	41	11·5
60/40	24	4·3	25	13·0
80/20	14	2·9	19	15·8
100/0	8	0·7	7	10·8

* Nineteen days' contact with saturated aqueous oxine (0·00035 M).

TABLE 5

Extraction of Organic Matter and Al *with Successive Treatments with 1% Oxine in 50% Acetone (from Sippy Creek Soil 813)*

Treatment	*Constituents removed with each extraction*	
	% *total organic carbon*	% *total* Al
1st extraction, 7 days . .	41	50
2nd extraction, 5 days . .	26	13
3rd extraction, 14 days . .	21	13
Total removed by three treatments . . .	88	76

colour of the supernatant liquid being greatest from the sample previously extracted in 80 per cent. acetone medium and least from the sample extracted in 20 per cent. acetone. No dispersion occurred from the sample treated in pure acetone solution. Although the amounts of C so dispersed were not estimated it seemed likely that some further dispersion of free organic matter occurred when solvent conditions were favourable. However, dispersion of the dried soils from the acetylacetone treatments in water released negligible amounts of organic matter irrespective of previous treatment, so that the effect noted in the oxine series may be specific for this reagent. Table 5 shows the effect of successive treatments on one portion of soil 813 using 1 per cent. oxine in 50 per cent. acetone. The results show that virtually complete extraction of organic carbon and of total Al has occurred and that the inhibition (either by oxine or acetone) is overcome if sufficient time is allowed for extraction.

The effect of reagent and of pH *on organic matter extractability*

It was reported previously (Martin and Reeve, loc. cit.) that from qualitative experiments the extractability of organic matter depended on the reagent used. The order of efficiency found in one series was cupferron > oxine > acetylacetone. The pH values of 0·2 M solutions of these reagents are respectively 7·1, 7·4, and 4·6 at 25° C. The enhanced efficiency of cupferron and oxine may thus be partly caused by their intrinsically higher alkalinity, quite apart from the fact that oxine, for example, forms stronger complexes than acetylacetone with many metals (Maley and Mellor, 1949). It was thought at this stage that valid comparisons of the extractive efficiency of chelating agents should be studied at the same arbitrary pH value for each compound tested.

In one experiment, samples of soil 813 were treated for 5 days with 0·2 M solutions of salicylaldehyde, acetylacetone, and oxine in 50 per cent. acetone at pH 4·8. Acetylacetone extracted considerable quantities of C, and salicylaldehyde (as expected) removed only traces of this constituent. Oxine at this pH was quite ineffective, the supernatant solution remaining clear throughout the experiment. It is noteworthy that about 4 ml. N H_2SO_4 per 100 ml. reagent were necessary to reduce the pH of oxine solution to the required value.

In a second trial, all three reagents were compared on soil 813 at pH 7·4 (equal to that of pure oxine in the same solvent) after 5 days as before; the pH values of salicylaldehyde and acetylacetone were adjusted with NaOH solution. A similar series, in which adjustments of pH to 7·4 were made with $Ca(OH)_2$, was studied concurrently, and included an oxine treatment in presence of $CaCl_2$ of equivalent molarity to the amount of $Ca(OH)_2$ used to adjust the pH of acetylacetone.

Table 6 shows that the efficiency of extraction in this series was in the order acetylacetone > oxine > salicylaldehyde, whether NaOH or $Ca(OH)_2$ was used for pH adjustment. Although salicylaldehyde, as expected, extracted least carbon the efficiency of the other two reagents was reversed from the order predicted from the known stability of their metal complexes (Maley and Mellor, loc. cit.). The effect of increased extraction time was not tested and might have influenced this order of extraction efficiency.

TABLE 6

Effect of Reagent on Extractability of Organic Matter at pH *7·4 on Sippy Creek Soil (813) in 50% Acetone*

	% *total* C *extracted*		% *total* C *extracted*
Salicylaldehyde*	9·4	Salicylaldehyde†	5·3
Acetylacetone*	43	Acetylacetone†	10·8
8-hydroxyquinoline	36	8-hydroxyquinoline‡	6·1

* pH adjusted with NaOH. † pH adjusted with $Ca(OH)_2$.
‡ 0·7 m.e. Ca^{++} added (≡ $Ca(OH)_2$ in acetylacetone).

Discussion

Bremner and Lees (1949) report in detail the extraction of organic N from four soils using alkali metal salts such as sodium citrate, oxalate and pyrophosphate, but found that only a small proportion of the total nitrogen (approximately 10 per cent.) was released by these compounds. These authors ascribe the action of their reagents to complexation of Ca^{++} (perhaps also with transition metal ions) which stabilize a portion of the organic fraction. A similar mechanism probably explains the extraction of organic matter from podzolic illuvial horizons reported in this paper, but from the results presented it seems that a very large proportion of the organic fraction in these soils is associated with, and stabilized by, Fe and Al.

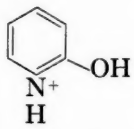
Gallagher (1942) reported a marked 'solubility' of the translocated humus of some Irish podzols in weak acids, particularly oxalic acid, and noted that podzol A horizons and samples of many other soil types yield negligible amounts of organic matter to these reagents, even on warming. The oxalate suspensions so prepared contained considerable amounts of Fe and Al. In qualitative experiments, we have confirmed Gallagher's results using oxalic and citric acids. Acetic acid is quite an inefficient extractor even at 1·0 N concentration so that, to be effective, weak acids must also form metal complexes as the pH of their solutions is probably not alone sufficient to displace Al or Fe from native organic matter.

It was implied in an earlier paper (Martin and Reeve, loc. cit.) that illuvial organic matter of podzols could be fractionated using successive treatments with reagents forming progressively stronger complexes with Fe and Al. This approach has been applied to the separation of proteins from blood plasma (Cohn *et al.*, 1950) and in an attempt to fractionate the Cu complexes of grassland herbage (Mills, 1954). The results reported here on the influence of reagent on extractability of organic matter suggest that, even if true metal coordination complexes exist in these soils, extraction of organic matter would be governed by other factors such as pH and the nature of the cation associated with the reagent (see Table 6). Even at the same pH value, however, the greater release of organic matter with Na-acetylacetone compared with oxine is probably caused by the dispersing effect of the Na ion present in the former. It seems at present that attempts to fractionate soil organic matter in this way would lack reality, since conditions which control the dispersion of organic colloids are probably as important as the breaking of metal-organic matter bonds in determining the final yield of material in suspension. By the same reasoning, it is possible that attempts to evaluate the role of pH on extractability would prove abortive unless all extractions were carried out in the presence of a constant salt background to offset the effect of the cation used in adjusting the pH values of the reagents.

Among the organic reagents studied so far, acetylacetone appears the most satisfactory; it is moderately miscible with water (approximately 12 per cent. by volume, or 1·2 M, at ordinary temperatures), possesses a favourable partition coefficient between water and ether or chloroform

and readily forms complexes with transition metals which are soluble in organic solvents. In particular, the chelates of Al and Fe are extremely stable; Izatt *et al.* (1955) give overall formation constants ($\log k_1 k_2 k_3$) of 22·3 and 26·2 for Al and Fe acetylacetonates respectively. A more detailed study of the extraction of organic matter with this reagent will be reported in Part II of this series.

Cupferron is not a satisfactory extractant as already discussed and the possible presence of this reagent in the final suspension throws doubt on the organic carbon determinations. Oxine is shown to be a slow extractor and no fully satisfactory reason for this behaviour can be advanced at this stage. Preliminary observations showed that although both 0·2 N H_2SO_4 and oxine, in acetone solution, separately extracted moderate quantities of organic matter from the Sippy Creek sample, a solution of oxine in 0·2 N H_2SO_4 containing acetone was a weak extractor and that the use of oxine-acetone solutions containing incremental amounts of H_2SO_4 resulted in progressively weaker extraction. This apparently synergistic effect, noted in a previous section in connexion with the further release of organic matter after oxine treatment, may be caused by the presence of the oxine cation



which would be favoured in acid solutions (Maley and Mellor, loc. cit.) and may partially flocculate the metal-free organic matter.

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CHEMICAL STUDIES OF PODZOLIC ILLUVIAL HORIZONS

II. THE USE OF ACETYLACETONE AS EXTRACTANT OF TRANSLOCATED ORGANIC MATTER

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Summary

A study of the effects of concentration of aqueous acetylacetone, extraction time, and of pH on the extraction of organic carbon and sesquioxides from four widely distributed podzol B horizons is reported. Reaction time has little influence on carbon extraction, but increasing reagent concentration causes, in general, an increase in carbon dispersion. Amounts of ether-extractable Fe and Al (removed as complexes of acetylacetone) increase directly with both concentration of reagent and time of contact. 0·2 M acetylacetone at pH 7 removes more carbon and in some cases more Al complex than at pH 4·2, but less Fe is extracted at the higher pH value. Pyrophosphate is more efficient than acetylacetone at the same concentration and pH, and tends to extract more Al and carbon, but less Fe. Sedimentation experiments suggest that the proportions of Al, Fe, and SiO_2 remaining in some organic-matter suspensions are physically distinct from the carbon fractions. An indurated iron-humus pan from New Zealand yielded very small amounts of ether-extractable Fe, suggesting that Al may play a predominant role in stabilizing the organic matter in this soil. Some of the extraction data given for the other soils suggest that Al is likely to act in this way and it is suggested that the function of Al in podzolization, previously assigned a secondary role, has possibly been overlooked.

THE advantages of acetylacetone over other organic chelating compounds as an extractant of soil organic matter from podzol B horizons have been enumerated in Part I of this series. The results of a more detailed investigation of the extractive properties of this reagent are reported in this paper.

Experimental

Four soils were selected for study; one of these (Beerwah groundwater podzol, no. 820) has been described in the previous paper. A brief description of the other samples is as follows:

(i) *Te Kopuru sand.* This is a strongly podzolized yellow-brown sand developed on consolidated coastal sand dunes near Kaiataia, N. Island, New Zealand (C. F. Sutherland, priv. comm.). The natural vegetation was formerly kauri forest. The illuvial horizon from this profile (24–36 in.) is dark brown in colour and is described as an indurated massive iron-humus pan; samples for study were supplied from the upper 6 in. of this horizon.

(ii) *Glendye* 5. This profile is an iron-humus podzol developed on granite till from Aberdeen, Scotland. Natural vegetation includes *Erica cinerea*, *Calluna* spp., and *Deschampsia flexuosa*; topography is steeply sloping (Glentworth, priv. comm.). The illuvial horizon (15–20 in.) is described as a dark brown, humus loamy sand with many coarse and fine roots.

(iii) *Woolnorth sand.* The B horizon (30–48 in.) from this profile, which is a ground-water podzol, is described by Hubble (1951) as a dark grey to black organic cemented sand pan. This soil is poorly drained and occurs on sandy heath country in north-west Tasmania. It is developed from fine siliceous sands of marine origin.

Extraction

Three concentrations of aqueous acetylacetone were used (0·2, 0·5, and 1·0 M) using BDH reagent grade material. For comparison purposes, solutions of 0·2 M acetylacetone at pH 7·0 (adjusted with NaOH), 0·2 M sodium pyrophosphate at pH 7·0, and 0·5 M NaOH were also used as extractants. Two extraction periods of 3 and 7 days were employed on separate soil samples, except for 0·5 M NaOH where 30 minutes extraction time was used.

Separate 2 g. portions of air-dry soil (< 2 mm.) were extracted with 50 ml. reagent, with occasional shaking, for the required period in stoppered 100 ml. centrifuge tubes. After centrifuging each soil residue was washed with water until clear, washed once with acetone (Woolnorth sample was washed repeatedly with acetone until a secondary release of organic carbon had ceased), and the combined extracts and washings extracted with ether overnight in a liquid/liquid extractor. Organic carbon, aluminium, and iron were determined in aliquots of the ether-free suspension, and aluminium and iron on the acid digest of the ether extract, as described in the previous paper. Total silica was determined gravimetrically using HF on each aqueous suspension. Silica determinations on all pyrophosphate extracts were unreliable, gains in weight being recorded in many instances following HF treatment of the ignited residue.

Results

Table 1 records the complete extraction data for the four soils and includes values for pH and clay content. The clay fraction of the Beerwah soil contains predominantly crystalline quartz, which may account for the low total Al content relative to clay. The clay from Te Kopuru soil contains kaolinite as the major constituent with a small amount of goethite; no X-ray data are available for the other two soils.

Organic carbon. The efficiency of dispersion of organic matter with acetylacetone as judged by the amounts of organic carbon found varied with soil type, but a considerable fraction of the total soil organic matter was removed from each sample by this reagent.

Time of contact (with acetylacetone alone) had less influence on organic-matter dispersibility than reagent concentration although the latter had little effect on the Te Kopuru sample. Comparing 0·2 M acetylacetone at pH 4·2 and 7·0, the neutral extractant was notably more efficient for all soils but had the least effect on Te Kopuru sand. The Woolnorth sand showed the lowest organic-matter dispersion at each level of reagent concentration, although a marked increase occurred on raising the pH. This soil was also unique in releasing further quantities of organic matter during acetone washing although the final water washing (prior to acetone treatment) was clear and colourless. Further work

TABLE I

Extractability of Organic Carbon, Sesquioxides, and Silica from Podzol B Horizons

(All constituents except SiO_2 expressed as % total in soil; SiO_2 expressed as % air-dry soil.)

Reagent / Time of extraction	*Acetylacetone* 0·2 M (pH = 4·18)				*Acetylacetone* 0·5 M (pH = 3·91)				*Acetylacetone* 1·0 M (pH = 3·75)				*Ac/ac* 0·2 M (pH = 7)		$Na_4P_2O_7$ (pH = 7)	0·5 M NaOH	*Total* % *air-dry soil*	pH	% Clay
	3 days		*7 days*		*3 days*		*7 days*		*3 days*		*7 days*		*3 days*		*3 days*	½ *hour*			
	*S**	*E*†	*S*	*E*	*S*	*E*	*S*	*E*	*S*	*E*	*S*	*E*	*S*	*E*	*S*	*S*			
Beerwah sand																			
Al	21	6	19	11	25	8	22	15	22	17	20	18	22	6	50	60	1·39		
Fe	8	20	8	28	10	21	11	32	8	32	7	34	10	15	27	44	0·18	4·6	14·5
C	60	..	66	..	87	..	82	..	88	..	87	..	81	..	90	97	2·71		
% SiO_2	0·47	..	0·39	..	0·96	..	0·67	..	0·82	..	0·49	..	..	..	..	..	..		
Te Kopuru sand																			
Al	27	4	24	6	27	7	27	9	30	5	29	11	24	3	27	35	4·15		
Fe	30	0·6	28	0·04	28	0·6	29	< 0·01	35	0·5	33	< 0·01	40	0·03	16	42	0·49	4·2	23·7
C	76	..	76	..	74	..	77	..	83	..	73	..	82	..	77	95	4·33		
% SiO_2	1·52	..	0·80	..	1·79	..	1·29	..	1·76	..	2·07	..	..	..	..	..	..		
Glendye 5																			
Al	22	..	26	21	22	25	25	29	24	30	22	31	4	25	51	64	2·75		
Fe	4	..	5	22	4	24	3	31	9	29	3	33	6	7	16	3	1·99	4·6	6·3
C	46	..	49	..	51	..	61	..	61	..	54	..	50	..	62	66	5·34		
% SiO_2	0·25	..	0·30	..	0·37	..	0·22	..	0·32	..	0·42	..	..	..	..	..	..		
Woolnorth sand																			
Al	21	21	11	18	17	19	17	25	29	25	29	32	3	31	72	62	0·32		
Fe	15	15	15	15	9	9	12	12	15	15	26	26	65	5	21	32	0·03	4·6	0·9
C	24	..	17	..	25	..	27	..	54	..	50	..	44	..	84	95	4·19		
% SiO_2	0·05	..	0·00	..	0·05	..	0·00	..	0·06	..	0·06	..	..	..	..	..	..		

* On suspension. † On ether extract.

showed that, after 17 per cent. of total carbon had been removed by a preliminary acetylacetone extraction, acetone washing removed a further 4–8 per cent. of total carbon immediately and 12–18 per cent. on standing in 50 per cent. aqueous acetone for some days. It was also observed that dehydration of the sample following acetylacetone treatment over silica gel *in vacuo*, followed by washing with anhydrous acetone, reduced the subsequent release of organic matter. Apparently the presence of water is necessary for the full effect, since suspension of the dried sample in 50 per cent. acetone showed that organic-matter release was eventually unimpaired. These observations resemble those of Gallagher (1942) who found that considerable quantities of organic carbon in the humus horizon of podzols could be 'dissolved' in organic solvents, but only after pretreatment to remove entrained silica.

Of the two inorganic extractants, NaOH was superior to sodium pyrophosphate as found by Bremner (1949), but in contrast to his results (which show a release of 20–26 per cent. of total organic N) practically all the carbon was dispersed from three of the samples after only 30 minutes' contact. Glendye 5 released two-thirds of its total carbon with NaOH in 30 minutes and only traces of the remainder dispersed on standing in 0·25 M NaOH for some days. The presence of roots in this sample may partly account for this discrepancy, since alkali is generally supposed to be without effect on plant residues.

Neutral pyrophosphate dispersed translocated organic matter very efficiently; 81–94 per cent. of that extracted by NaOH was removed by this reagent. By contrast neutral 0·2 M acetylacetone released only 46–86 per cent. of the NaOH-soluble organic matter. Woolnorth sand showed a twofold increase in recovery of organic matter with pyrophosphate compared with acetylacetone at the same pH.

Aluminium. By contrast to the dispersion of organic matter, both extraction time and reagent concentration directly affect the amounts of this metal extracted by ether as acetylacetone complex. The proportion of total Al extracted in this way varies with soil type but is generally of a lower order than the corresponding proportion of total carbon. Aluminium remaining in the organic-matter suspension was fairly constant for each soil irrespective of the amounts of carbon released or the amounts of Al extracted by ether. The ratios of carbon dispersed to ether-soluble aluminium were not constant for any one soil; there was a tendency towards narrower C/Al ratios as more Al was extracted, but this effect cannot be consistently related to treatment. The effect of higher pH resulted in an increase in ether-soluble Al in two of the soils and a slight decrease (probably not significant) in the other two.

Pyrophosphate extracted a large and in most cases a major fraction of the total soil Al. Except for Te Kopuru sand, pyrophosphate-soluble Al was greater than the sum of the ether-soluble and suspension-Al in the acetylacetone series at pH 7. This increase could not be correlated with clay content (so that it is unlikely that clay minerals had suffered appreciable breakdown by pyrophosphate) and could be attributed to partial solution of free hydrous aluminium oxide. Alkali removed slightly more Al than pyrophosphate in three of the soils.

Iron. Except for the New Zealand sample the extraction of Fe with acetylacetone resembled the release of Al in that both time of contact and reagent concentration directly affected extractability of the ether-soluble ferric acetylacetonate. Very small amounts of this complex were extracted from Te Kopuru sand irrespective of pH, concentration, or time of contact. Neutral acetylacetone extracted less iron complex than the more acid reagent, supporting unpublished results obtained in this laboratory which show that freshly prepared hydrous ferric oxide dissolves less in acetylacetone with increase in pH. Pyrophosphate tends to extract smaller amounts of iron than neutral acetylacetone in two soils (sum of ether-soluble and suspension Fe). Alkali extracted more Fe with one exception, in which very small amounts were recovered from Glendye 5 with this reagent.

Iron remaining in suspension after ether extraction was not dependent on extraction conditions and remained reasonably constant for each soil type.

Silica. The amounts of silica present in the organic-matter suspensions were not correlated with extraction conditions or with the amounts of carbon or iron removed. There was a slight degree of correlation between SiO_2 and Al in suspension suggesting that part of the silica may have been present as clay minerals.

Sedimentation experiment

It was of interest to investigate, in an empirical manner, possible associations between the four major constituents present in each organic-matter suspension. Two soils (Te Kopuru and Beerwah) were treated with acetylacetone, the centrifuged suspensions ether-extracted and (after evaporation of ether) placed in stoppered polythene bottles in a constant temperature room at 20° C. A few drops of chloroform were added to the bottles to prevent microbial growth. After thorough initial shaking, 20 ml. samples were withdrawn from the top 1–2 cm. layer from each suspension at selected time intervals and by analysis on aliquots of each pipette sample the variation in relative concentrations of each constituent could be determined during sedimentation. Silica was determined colorimetrically, after fusion of the evaporated residue in Na_2CO_3, by the method of Corey and Jackson (1953). Table 2 summarizes the results obtained. In the Beerwah sample, no change in

TABLE 2

Relative Change of Constituents in Two Organic Matter Suspensions during Sedimentation

(Results expressed as % of initial value obtained)

	Beerwah sand				*Te Kopuru sand*			
Sedimentation time, days	C	Al	Fe	SiO_2	C	Al	Fe	SiO_2
0	100	100	100	100	100	100	100	100
4	103	95	87	..	95	76	95	78
7	103	85	..	..	92	62	84	48
33	98	88	60	87	76	38	49	72

concentration of organic carbon occurred for 33 days, but Fe dropped to nearly half its original value in this time. At least 40 per cent. of the Fe in suspension is, therefore, not physically associated with organic carbon. Al and SiO_2 show very slow sedimentation rates, but their decrease appears to be correlated. Carbon in the New Zealand soil suspension showed definite decrease in concentration, but both Fe and Al decreased more rapidly. Most of the SiO_2 figures show some degree of correlation with Al, but the 33-day value for SiO_2 is probably the result of contamination. In view of the relative densities of Fe_2O_3 (5·2) and Al_2O_3 (approximately 3·5) it is surprising that the Fe concentration should decrease more slowly than that of Al, although the respective particle size distribution may be widely different.

Discussion

It is apparent from the extraction data that only a fraction of the total sesquioxides in each soil is involved in stabilizing the B horizon organic matter. Further, it is likely (from considerations given in Part I of this series) that the proportion of each metal extracted as the acetylacetone complex represents the 'active' fraction, removal of which causes dispersion of organic carbon. In the four soil types studied, this means that a relatively small fraction of either metal is directly attached to, and responsible for the precipitation of, a major part of the organic fraction.

The results show that acetylacetone is a highly efficient extractor of translocated organic matter in podzol soils; in this respect pyrophosphate was markedly superior at neutral pH in only one of the samples studied. The fact that the hypothetical 'active' fraction can be isolated by ether extraction is one advantage, and (as pointed out in Part I) obviates the need for dialysis which is likely to cause large losses of organic carbon from some pyrophosphate extracts; these considerations suggest that, in spite of its lower extracting power, acetylacetone is to be preferred for certain types of study. The superiority of pyrophosphate (at the same pH and concentration of reagent) is difficult to explain in terms of chelate stability; e.g. Martell and Calvin (1952) report the overall (log) stability constants of Cu pyrophosphate and Cu acetylacetone as 10·1 and 17·4 respectively (the latter value from measurements in 50 per cent. dioxane); acetylacetone should thus be more efficient in extraction of carbon and sesquioxides. The real explanation may lie in the fact that acetylacetone at pH 7 contains only 1–2 per cent. free anion and the Na^+ concentration is low, so that metals removed from the organic matter are replaced predominantly by H^+; with $Na_2H_2P_2O_7$, degree of ionization is large and a larger fraction of the active groups on the organic matter surface is replaced by Na^+, resulting in greater dispersion.

The results of the sedimentation experiment are variable but suggest that in Beerwah and Te Kopuru organic-matter suspensions part of the sesquioxides and silica are physically distinct from the organic carbon. If some of the entrained sesquioxides are still attached to organic carbon (whether sorbed or present as chelates) they clearly do not function as precipitants. The high dispersion of most of the organic-matter suspensions and their stability at room temperature has been repeatedly

observed. It is probable that the amounts of silica and sesquioxides in suspension (also clay minerals if present) may largely depend on conditions of centrifuging and washing. No attempt has yet been made to free the preparations completely from extraneous inorganic material, although it has been observed that shaking with H-amberlite can remove over 90 per cent. of entrained Al from the Beerwah horizon.

In view of the fact that acetylacetone and pyrophosphate dissolve free hydrous oxides of iron and aluminium to some extent it cannot be concluded that the quantity of metal complex extracted represents the net amount of metal precipitating the organic matter, but at least the true active fraction cannot exceed this value. The amounts of Al complex extracted by ether from all suspensions prepared with acetylacetone markedly exceed the corresponding amounts of ether-extractable Fe in three of the soil types studied, and although in the Glendye 5 soil the extractable Al/Fe ratio is narrower, Al still often exceeds Fe. This may be a reflection of the excess of total Al over total Fe present in all the soils and it is, therefore, difficult to decide which metal has the predominant influence in combining with the organic fraction. It is noteworthy that increasing the pH of 0·2 M acetylacetone caused a reduction in ether-extractable Fe in every soil but an increase in organic matter extraction. Aluminium is not appreciably affected and in the Woolnorth sand the higher pH value gives rise to an increase in ether-extractability of Al accompanied by a two-fold increase in organic carbon extraction.

The results from the Te Kopuru organic horizon are of particular interest. From the very low amounts of acetylacetone complex extracted with ether it seems that Fe plays little or no part in stabilizing organic matter in this soil; it is concluded that Al is probably the 'active' metal even though the ether-soluble fraction accounts for only 5–10 per cent. of the total soil Al. If this tentative conclusion is correct it is interesting to speculate on the relative importance of Fe and Al in the later stages of the podzolization process. Almost all previous work has tried to account for the observed horizon differentiation in terms of the mutual interaction of iron and 'humus', aluminium being accorded a secondary role. As pointed out by Deb (1949) the pH values of most podzol horizons preclude the presence of free Fe^{+++} ions, and the insolubility of iron-organic matter colloids in the B horizons must be accounted for either by mutual coagulation or by complex-formation. A consideration of the latter alternative will be the subject of Part III of this series, but meanwhile the possibly predominant role of Al in precipitation of organic matter in the B horizon seems to have been overlooked. Al^{+++} ions are completely precipitated at about pH 5 so that $Al(OH)_2^+$, $Al(OH)^{++}$ and possibly a small amount of Al^{+++} ions are present in these horizons and could function as the active means of precipitation. The concomitant presence of Fe must still be accounted for, and the mutual flocculating properties of Fe and humus sols studied by Deb will be extended to Al solutions and will be the subject of further studies.

Explanations of the action of alkali in dispersing soil organic matter suggest depolymerization of large organic matter 'molecules' as a prerequisite to extraction. It is also likely that hydrogen bonds (postulated

by Halla and Ruston (1955) to be present in synthetic humic acids) may be destroyed in strong alkali, leading to increased dispersion. However, the fact that 80–90 per cent. of the organic matter extracted by NaOH is also extracted by pyrophosphate suggests that the main action of NaOH on these soils is to form aluminate anions, preventing the flocculating action of Al^{+++} cations and leading to ready dispersion of the organic carbon.

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STUDIES ON SOIL MANGANESE

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Summary

1. While results of extractions, performed in the presence of reducing agents, of mineral soils low in organic-matter content suggested that manganese higher oxides approaching the manganese-dioxide type are present or formed by oxidation of added manganese, results obtained with other extractants lend support to the suggestion by Dion and Mann that hydrated manganese oxides may occur in such soils.

2. From the distribution of manganese in various extracts of alkaline organic soils with or without added manganese materials, it was concluded that no difficultly reducible higher oxides of manganese are present or formed. Some evidence was presented for the view that manganese of a higher valency form may remain in combination with the organic matter or may be retained in this manner after oxidation of added manganese.

3. Divalent manganese present as a complex of the organic matter of alkaline organic soils could be estimated by extraction with a monocalcium disodium versenate solution. It constituted 10–20 per cent. of the total manganese content. Manganese added to such soils and not present as readily soluble manganese was recovered by this extractant shortly after application; manganese did not, however, remain in this form after some weeks' contact with soils.

4. The organic matter of various soluble organic-matter fractions migrated anionically over a wide pH range; that of lignin solutions remained at the isoelectric point. Manganese already present in soluble organic-matter fractions migrated anionically in contrast to manganese added and retained by such fractions that moved predominantly as a cation.

5. The oxidizable carbon or total nitrogen content of soluble organic-matter fractions was not closely related to the amounts of manganese retained by such fractions in a form that was non-dialysable against potassium chloride. Some evidence was obtained that different types of complexing groups may be present in water extracts subsequent to extraction by sodium chloride of an alkaline fen and of an acid raw-humus peat.

MANGANESE deficiency in plants has long been associated with neutral or alkaline organic soils. Since the view was generally held that the plants probably assimilate manganese in the divalent form, it was tentatively suggested in previous work (Heintze and Mann, 1949) that, on organic soils containing substantial amounts of total manganese but insufficient amounts of available manganese, part of the manganese occurred as divalent manganese complexed by the organic matter. This form might be dissociated to such a slight extent that the amount of manganese in the soil solution becomes insufficient for the need of plants. Several workers (Jones and Leeper, 1951; Heintze, 1956) have since shown that manganese higher oxides are potential sources of available manganese and that their availabilities in some cases are correlated with their reducibilities by hydroquinone. The present work is partly an attempt to define the manganese higher oxides in, or formed after addition of manganese to, alkaline soils by comparing different manganese fractions of such soils with and without added manganese materials. Various extractants were used to estimate sparingly soluble divalent

manganese retained in a complex form by the organic matter. The nature of such manganese was investigated by observing the order of migration in electrophoresis and by estimating the non-dialysable manganese fractions in dialysis against potassium chloride of manganese present in, or added to, soluble organic-matter fractions.

Materials and Methods

X-ray analysis of manganese higher oxides of the type hausmannite and manganite prepared according to Feitknecht and Marti (1945) confirmed that their structures corresponded to those of the naturally occurring minerals hausmannite and manganite. 'Manganous manganite' was prepared by precipitation from a solution of calcium permanganate by the slow addition of manganese sulphate solution. This preparation possessed a structure similar to γ manganese dioxide. Hydrated colloidal manganese dioxide was prepared as previously described by Heintze and Mann (1949) by dismutation of trivalent manganese in pyrophosphate. The *n*-values of hausmannite, manganite, 'manganous manganite', and hydrated manganese dioxide were 1·35, 1·48, 2·06, and 2·0 respectively. The minerals pyrolusite, hausmannite, and manganite were also used.

Soils

Soils were chosen to give a wide range of organic-matter contents, and were neutral or alkaline in reaction. Several samples from the same place were used, and names refer therefore to areas only.

Manganese fractions and determination

Exchangeable, pyrophosphate- and versenate-soluble manganese were estimated by extracting soils with neutral M-ammonium acetate, M/5 pyrophosphate, or M/5 versenate solutions of pH 7·0 or 9·4. Manganese reducible by hydroquinone or hydrosulphite was estimated as described earlier (Heintze and Mann, 1951). The separate reduction and extraction method was similar to that used by Jones and Leeper (1951), but using 0·2 per cent. hydroquinone. In all extractions the soil : solution ratio was 1·20 and extraction, when not otherwise stated, was 18 hours with intermittent shaking. Manganese in all extracts was determined colorimetrically as permanganate after oxidation with periodate.

Soil nitrogen was determined by a micro-Kjeldahl procedure using Markham's (1942) still, and *oxidizable carbon* was estimated by oxidizing extracts with permanganate in acid solution.

Organic-matter fractions

Various fractions of soluble organic matter were obtained by extracting soils with normal sodium chloride several times before consecutive extractions with water, M/5-alkaline pyrophosphate and 2 per cent. sodium hydroxide. These extracts were sometimes concentrated by vacuum distillation. Various humic-acid preparations were obtained by the usual reprecipitation technique from extracts of alkaline fen soils, by neutral 0·1 M. sodium pyrophosphate or oxalate, 1 per cent. sodium fluoride or 2 per cent. sodium hydroxide. Neutral 'lignin' solution was

obtained by dissolving and dialysing a commercial lignin preparation, Meadol.

Paper electrophoresis

M/10 sodium acetate at various pH values was used as electrolyte. The current was 4–6 milliamp. and the duration 4–5 hours. The paper was then 'developed' for manganese by spraying with sodium periodate followed by tetramethyldiaminodiphenylmethane ('tetra base') solution or with benzidine acetate after sodium hydroxide. Mixtures of manganese and soluble organic-matter fractions, humic-acid or lignin preparations were shaken for 1 hour and dialysed against water before use.

Dialysis

Mixtures of increasing amounts of manganese added to various soluble organic-matter fractions were shaken for one hour and afterwards dialysed against a tenfold volume of M/10 potassium chloride for 24 hours. The dialyses were sometimes continued against a fresh solution of potassium chloride. Some dialysates were strongly coloured denoting the presence of dialysable organic matter of the extracts. Such extracts were predialysed before adding manganese.

Results

Manganese higher oxides in neutral or alkaline soils

Extractions of manganese higher oxides. The amounts of manganese extracted by various extractants from different manganese higher oxides, and the effect of adding an alkaline fen soil to the oxides before extraction

TABLE 1

Percentage Recovery of Manganese added as Synthetic or Mineral Manganese Higher Oxides by Various Extractants in the Absence or Presence of an Alkaline Fen Soil

2.0 mg. manganese in 50 ml. solution was used without soil.
600 p.p.m. manganese was used when soil was present.

	Percentage recovery of added manganese by:							
	AmAc HQ		AmAc HS		HQ–$Ca(NO_3)_2$		Pyrophosphate pH 9·5	
	Without soil	*With soil*	*Without soil*	*With soil*	*Without soil*	*With soil*	*Without soil*	*With soil*
Colloidal hydrated manganese dioxide (synthetic)	96	43	96	57	98	70	0	24
'Manganous-manganite' (synthetic) (MnO_2)	95	40	95	57	95	70	0	25
Manganese dioxide, pyrol[illegible]e, mineral	95	..	95	..	97	..	0	..
Hausmannite (synthetic)	90	44	97	51	24	14	30	15
Hausmannite (mineral)	2	..	21	..	..	..	..	..
Manganite (synthetic)	82	32	86	58	10	2	8	2
Manganite (mineral)	14	..	60	..	..	..	0	..

are set out in Table 1. Reducible manganese was estimated after extraction with M neutral ammonium acetate containing either hydroquinone (AmAc HQ) or hydrosulphite (AmAc HS) or by the separate reduction method [HQ–$Ca(NO_3)_2$]. Manganese extracted by alkaline pyrophosphate was also estimated.

Manganese higher oxides of the dioxide type were extracted equally well by all solutions containing reducing agents. The more difficultly reducible oxides, hausmannite and manganite in mineral form, yielded more manganese in extracts of ammonium acetate containing hydrosulphite, than in those containing hydroquinone, while equal amounts of manganese were found in these extracts from the same but freshly prepared oxides. Similar but considerably lower amounts of manganese were extracted from the synthetic hausmannite and manganite by the separate reduction and extraction method and by alkaline pyrophosphate. No manganese was extracted by alkaline pyrophosphate from the manganese dioxides alone, but a quarter of the manganese was recovered from these oxides in the presence of soil owing to reduction by dissolved organic matter. In the presence of the fen soil, less manganese was extracted from all oxides by the other extractants.

Extraction of various manganese materials after incubation with soils. To obtain information on the types of manganese higher oxides formed when manganese salts have been in contact with neutral or alkaline soils for some time, various manganese fractions were estimated after incubation of some soils with manganese sulphate and known manganese higher oxides. The soils were all alkaline and represented mineral soils low in organic matter (Rothamsted), loam soils with recently applied manure (Marston), and fen soils (Burwell).

The soils were mixed with the manganese materials and, after adding water to bring the moisture content up to 40 per cent. of the water-holding capacity, they were kept at room temperature for 3–4 weeks with occasional shaking. The soils were then air-dried and extracted with the same extractants as were used in previous experiments. The results are set out in Table 2.

The distribution of manganese in the various extracts of the mineral soil low in organic matter with added manganese salt suggested that in such soils oxidation of manganous manganese leads to a manganese higher oxide of the dioxide type. The separate reduction and extraction remained, as in the previous experiment, the best extractant of manganese added as manganese dioxide to a fen soil. More manganese added as sulphate was extracted by this method than by ammonium acetate containing hydrosulphite, suggesting that manganese sulphate had not been converted to difficultly reducible manganese higher oxides. While the above results support the view that oxidation of added manganese salts leads to the manganese dioxide type of oxide, the comparison of recovery values of various manganese materials in alkaline pyrophosphate do not agree with this view. It was found that the recovery by alkaline pyrophosphate of manganese added as sulphate to the fen soil was substantially higher than that of manganese added as highly reactive manganese dioxide; it was equal to the recovery by separate reduction and extraction of manganese added as sulphate. It would therefore seem possible that at least part of the divalent manganese added to the fen soil had been oxidized to a higher valency form of manganese in combination with organic matter.

The higher recovery values in alkaline pyrophosphate extracts of

manganese added as dioxides to the loam soil as compared with recovery when the same manganese material was added to the highly organic fen soil suggested differences in the organic-matter fractions soluble in this extractant. Such differences could be shown by comparing the respective reducing capacities of the two soils, estimated by the amounts of

TABLE 2

Recovery of Manganese from 600 p.p.m. Mn added as Manganese Sulphate or Synthetic Manganese Higher Oxides to Soils by Various Extractants after Incubation

Soils	*Rothamsted*	*Marston*	*Burwell*
Organic carbon mgs. C/g. soil . .	36·5	71	272
pH	8·2	7·4	7·4
	Percentage recovery of added manganese		
Addition of:			
(I) *Manganese sulphate*			
Am Ac HS	85	52	45
Am Ac HQ	91	41	30
HQ–$Ca(NO_3)_2$	78	77	64
Pyrophosphate pH 9·5 . .	0	65	66
(II) *Colloidal hydrated manganese dioxide*			
Am Ac HS	87	52	45
Am Ac HQ	92	50	28
HQ–$Ca(NO_3)_2$	90	54	59
Pyrophosphate pH 9·5 . .	0	52	27
(III) '*Manganous manganite*' (γ-MnO_2)			
Am Ac HS	85	57	48
Am Ac HQ	85	60	25
HQ–$Ca(NO_3)_2$	90	73	77
Pyrophosphate pH 9·5 . .	0	43	27
(IV) *Hausmannite*			
Am Ac HS	69	58	32
Am Ac HQ	50	35	16
HQ–$Ca(NO_3)_2$	14	0	11
Pyrophosphate pH 9·5 . .	10	16	8
(V) α-*Manganite*			
Am Ac HS	40	50	14
Am Ac HQ	0	13	11
HQ–$Ca(NO_3)_2$	0	3	3
Pyrophosphate pH 9·5 . .	2	8	2

manganese dioxide reduced by the pyrophosphate extracts of the untreated soils. The reducing capacity of the loam soil was found to be considerably greater than that of the fen soil.

Extraction of manganese higher oxides of untreated soils. Alkaline soils varying in their organic-matter content were extracted with the above extractants in an attempt to define the type of manganese higher oxides likely to occur in such soils. The methods were also compared as means for estimating manganese availability. The results are summarized in Table 3.

The distribution of manganese in the various extracts of mineral soils low in organic matter supported the assumption that the manganese higher oxides were of the dioxide type. More manganese was extracted from the organic soils by hydroquinone followed by calcium nitrate than by the stronger reducing agent hydrosulphite in ammonium acetate. It seems, therefore, unlikely that more difficultly reducible manganese higher oxides are present in these soils. On a few organic soils, the

TABLE 3

Manganese Extracted from Mineral and Organic Soils by Extractants Containing Hydroquinone or Hydrosulphite and by Alkaline Pyrophosphate

Mineral Soils	pH	*Nitrogen mg./g.*	*Organic carbon mg./g. soil*	*Total manganese p.p.m.*	*Percentage of total manganese extracted by:*			
					AmAc HQ	HQ–$Ca(NO_3)_2$	AmAc HS	*Pyrophosphate* pH 9·5
Kent	7·4	..	4·7	190	20	26	30	12
Rothamsted	8·4	1·05	6·5	1,800	67	65	67	3
Norfolk	7·5	1·60	8·3	700	55	57	56	24
Kent	7·6	..	50	190	19	25	30	13
Devon	7·8	..	..	240	17	55	50	43
Organic soils								
Swaffham	7·6	..	96	245	12	26	15	17
Isleham	7·2	8·5	140	165	12	31	26	20
Swaffham	7·2	13·4	162	238	5	28	20	17
Swaffham	7·4	18·9	240	470	31	66	51	65
Burwell	7·9	16·9	292	143	7	41	10	28

greater part of the total manganese could be extracted either by alkaline pyrophosphate or by the separate reduction and extraction method. This result is similar to that obtained after manganese sulphate had been incubated with a fen soil. In general, however, only a small part of the total manganese was extracted by alkaline pyrophosphate. The results confirm an earlier suggestion (Heintze and Mann, 1951) that the larger amounts of manganese extracted by ammonium acetate containing hydrosulphite instead of hydroquinone is due to more effective exchange between reduced manganese in the soil and ferrous ions present in the former but absent in the latter extracts, and are not due to the occurrence of more difficultly soluble manganese oxides.

Applying the above extractions to a group of alkaline organic soils, it was found that the occurrence of manganese deficiency symptoms in crops on the soils was associated with low values for several variables: total manganese, the absolute quantities and the fractions of total manganese extracted by the above extractants. No single fraction of the soil manganese was found to give an adequate estimate of availability.

Attempts to extract divalent manganese held by soil organic matter

1. *Extraction with ammonium acetate containing copper sulphate.* Heintze and Mann (1949) showed that while ammonium acetate containing copper-salts was a better extractant of manganese present or added to organic soils than was ammonium acetate alone, colloidal manganese dioxide added to such soils was reduced by the former extractant. From

results obtained when manganese higher oxides were extracted with copper salts Hemstock and Low (1953) concluded that the increases found by Heintze and Mann were due, therefore, to 'exchange' between cuprammonium ions and manganese in chelated form with the organic matter. The following experiment, however, does not bear out their suggestion.

An alkaline fen soil which had been extracted with an aqueous solution of hydroquinone, and washed repeatedly on the centrifuge to remove surplus hydroquinone, was divided into two parts. One half was extracted once with neutral M ammonium acetate containing 0·02 N copper

TABLE 4

Reduction of Higher Manganese Oxides of a Manganiferous Mineral Soil by Alkaline M/5 Pyrophosphate and M/5 Versenate Soil Extracts

	Initial Mn *content* (mg. Mn/20 ml.) *of extract*	*Increase after treatment with 1 g. soil* mg. Mn/20 ml.
Pyrophosphate alone	Nil	0·02
Versenate alone	Nil	0·01
Pyrophosphate extracts		
Burwell Fen	0·04	0·15
Methwold Fen	0·22	0·39
Versenate extracts		
Burwell Fen	0·03	0·005
Methwold Fen	0·10	0·01

sulphate, the pH being maintained at 7·0, whilst the other half was extracted three times with neutral M/2 calcium nitrate. The two extractants contained 200 and 190 p.p.m. manganese respectively. The untreated soil extracted with ammonium acetate with or without added copper salt and with calcium nitrate yielded 165, 3, and 8 p.p.m. manganese respectively. Thus, while the increase in manganese in extracts of ammonium acetate containing copper sulphate after reduction by hydroquinone was from 165 to 190 p.p.m., the corresponding increase of the more exhaustive extraction with calcium nitrate was from 8 to 200 p.p.m., implying that reduction had taken place in the ammonium acetate containing copper sulphate extracts.

2. *Extraction with versenate and pyrophosphate solutions.* Alkaline pyrophosphate was used in earlier work (Heintze and Mann, 1949) in attempts to extract divalent manganese held by soil organic matter. It was, however, shown that under the conditions used some reduction could take place. Preliminary experiments (Heintze, 1956) with versenate instead of pyrophosphate as extractant were extended. While alkaline sodium versenate solutions were found to extract up to 80 per cent. of the total manganese of some fen soils, it was obvious from the colour of the soil extract that considerable amounts of the organic matter had been dissolved. By using disodium monocalcium versenate instead, extracts were obtained which for most soils were no darker in colour than corresponding ammonium acetate extracts. Such versenate solutions

recovered about 90 per cent. of divalent manganese added to organic alkaline soils, if extractions were made before any oxidation had taken place. The solubilities of various manganese higher oxides in versenate extracts were low; thus of 2·5 mg. manganese added as the minerals manganite, hausmannite, and pyrolusite to 50 ml. M/5 neutral versenate solution, 0, 10, and 5γ were dissolved, respectively, after 16 hours. To ascertain whether reduction of manganese higher oxides present in soils took place to any considerable extent during versenate extractions, the following experiment was made.

Two alkaline fen soils were extracted with either alkaline pyrophosphate or versenate solution. The manganese content of part of the extracts was estimated. Another part of the extract (20 ml.) was used to extract one gram of a manganiferous mineral soil overnight (Table 4).

The pyrophosphate extracts of the fen soils, allowing for their manganese contents, extracted more manganese from the mineral soil than did the pyrophosphate alone. The increase in manganese thus represented reduction of manganese higher oxides of the mineral soil. In contrast to the results obtained with pyrophosphate, only small increases of manganese were obtained after versenate extracts had reacted with

TABLE 5

Manganese Extracted by M/5 Disodium Monocalcium Versenate and M/5 Pyrophosphate from Alkaline Soils in 2 and 18 hours

Soils	Total manganese p.p.m.	p.p.m. Manganese					
		18 hours				2 hours	
		Versenate		Pyrophosphate		Versenate	Pyrophosphate
		pH 7·0	pH 9·2	pH 7·0	pH 9·4	pH 7·0	pH 9·4
Mineral soils							
Rothamsted (Barnfield 8:0)	1,550	35	40	310	40	32	35
,, (,, 1:0)	1,200	40	..	260	40	38	40
Gold Coast	2,200	160	..	460	130	..	..
Organic soils							
Methwold Fen, Cambridge	900	100	115	..	390	95	95
Swaffham Fen, Norfolk	470	87	100	..	306	75	80
Swaffham Fen, Norfolk	240	30	33	..	42	28	30
Burwell Fen, Cambridge	160	30	..	..	35	30	30
Holme Fen, Lincoln	274	55	60	..	110	50	55

the mineral soil. The low reducing action of versenate extracts of organic soils was also shown by a large increase in the manganese extracted from an alkaline fen by a versenate solution containing 0·2 per cent. added hydroquinone, namely from 65 to 520 p.p.m. The values obtained in alkaline pyrophosphate remained unaltered by addition of hydroquinone. A number of alkaline mineral soils low in organic matter, and a number of organic soils were extracted for either 18 hours or 2 hours with M/5 pyrophosphate or M/5 versenate solutions. Typical results are set out in Table 5.

From manganiferous mineral soils low in organic matter, neutral or alkaline versenate solutions extracted amounts of manganese similar to those extracted by alkaline pyrophosphate, but considerably smaller amounts than neutral pyrophosphate. These latter extracts contained

trivalent manganese, while neutral versenate extracts did not. The reverse dismutation reaction takes place in neutral pyrophosphate solutions containing divalent manganese in the presence of manganese dioxide according to the equation:

$$Mn^{2+} + MnO_2 + 4H^+ \longrightarrow 2Mn^{3+} + 2H_2O$$

This reaction was shown in earlier work (Heintze and Mann, 1949) to take place also in the presence of manganiferous mineral soils. In neutral versenate solutions containing divalent manganese, no reverse dismutation took place in the presence of hausmannite, pyrolusite, or manganite as minerals nor in the presence of precipitated manganese dioxide or manganiferous mineral soils. When hydrated colloidal manganese dioxide, on the other hand, was treated with neutral versenate solutions containing divalent manganese, the manganese dioxide dissolved, giving rise to trivalent manganese in amounts corresponding to twice the added divalent manganese. It would therefore seem that if manganiferous soils contain manganese compounds approximating to manganese dioxide, these are not similar in reactivity to hydrated manganese dioxide.

The results obtained with manganiferous mineral soils low in organic-matter content showed that the effect of shortening the reaction time on the alkaline pyrophosphate-soluble manganese was small. In these soils this fraction often constituted less than 10 per cent. of the total manganese present. Most soils yielded similar amounts of manganese in long and short extractions with versenate, with the exception of some mineral soils with recently added organic matter. Since, if hydrated manganese dioxide was added to a fen soil and the soil mixture extracted with alkaline pyrophosphate for 2 hours, less than 1 per cent. of the added manganese was recovered by the pyrophosphate, and since similar values were obtained by short-time extractions with versenate and pyrophosphate, it would seem justified to regard the amounts of manganese removed by these extractants from alkaline organic soils as representing divalent manganese complexed by the organic matter. This form of soil manganese constituted for a number of soils about 10–20 per cent. of the total manganese. Compared with the manganese fraction obtained by separate reduction and exchange, the pyrophosphate fraction was considerably smaller for some soils. It was further found that manganese salts added to alkaline organic soils and present in a sparingly soluble form shortly after application, could be recovered to the extent of about 90 per cent. by versenate extractions. This extractant was, however, unsuccessful in recovering added manganese when the manganese salts had been allowed to react with the soils for a long period. In earlier work (Heintze and Mann, 1949) it was shown that considerable amounts of divalent manganese added in M/5 neutral, but not in M/5 alkaline, pyrophosphate were retained by alkaline organic soils. In similar experiments using neutral versenate solutions, no retention was obtained even at high dilution (M/3000) of the versenate.

Manganese complexes with organic matter

Since the existence of manganese complexed by organic matter had

been evidenced by the foregoing results, an attempt was made to investigate the nature of such manganese by observing the order of migration during electrophoresis, and by estimating the fraction of manganese, non-dialysable against potassium chloride, present in or added to soluble organic-matter fractions and humic-acid preparations.

Electrophoresis. The organic matter of soluble fractions and of humic-acid preparations was found to migrate anionically over a pH range of 4–9, forming a light brown band. Lignin solutions, on the other hand, remained at the isoelectric point over this pH range. Organic matter

TABLE 6

Order of Electro-migration of Manganese Present in Various Soil Extracts or Added to such Extracts or to Humic-acid and Lignin Preparations. Electrolyte: neutral 0·1 M sodium acetate

Solution	pH *of solution*	*Order of migration of manganese*		
		Towards cathode	*Isoelectric point*	*Towards anode*
A. *Soil extracts*				
Water	8·9	−	−	+
,,	6·0	−	−	+
Alkaline pyrophosphate	9·2	−	−	+
,, ,,	7·2	−	−	+
Sodium hydroxide	11	−	+	−
,, ,,	7·3	−	+	+
B. *Manganese added to extracts and dialysed against water*				
Water	7·8	+	−	+
Pyrophosphate	7·2	+	−	+
Sodium hydroxide	8·0	+	+	−
C. *Manganese added to various humic-acid preparations and dialysed against water*				
Humic acid precipitated from:				
Sodium fluoride extracts	6·2	+	−	+ (faint)
	7·6	+	−	+ (faint)
Pyrophosphate extracts	5·4	+	−	+ (faint)
	8·4	+	−	+ (faint)
Sodium hydroxide extracts	10·0	+	+	−
	6·8	+	+	−
	8·5	+	+	−
D. *Manganese added to lignin preparations. Manganese mixtures dialysed*				
'Meadol'	7·1	+	+	−
Auto-oxidized, ammoniated 'Meadol'	7·0	+	+	−
'Meadol'-edestine mixture	7·5	+	+	−

dissolved in sodium hydroxide extracts was found both at the initial point and on the anodic side. The electrophoretic behaviour of manganese present in, or added to, various extracts, humic acid or lignin preparations, is set out in a summarized form in Table 6.

In neutral or alkaline water extracts of organic soils saturated with sodium, manganese always migrated anionically together with organic

matter. In water extracts of some soils, two separate manganese areas were distinguishable; and subsequent treatment with pyrophosphate gave similar results. In the pyrophosphate extract the distance of the manganese spot farthest away from the origin was the same as that obtained with a manganese pyrophosphate solution. Judging from the size and intensity of the two manganese areas from these soil extracts, it would seem that the greater part of manganese in them occurred as pyrophosphate. Pyrophosphate extracts of soils that had not been previously extracted, gave the same results. In sodium hydroxide extracts, manganese together with organic matter, remained at the isoelectric point, while some manganese migrated anionically after acidifying such extracts. Cationically migrating manganese was found over a wide pH

TABLE 7

Manganese Present before and after Dialysis of Mixtures of Various Soluble Organic-matter Fractions and Humic Acids with Increasing Amounts of Manganese

Solutions	*Manganese present* γ Mn/ml.			
	pH *of mixture*	*Before dialysis*	*After dialysis*	*Oxidizable carbon* mg. C/ml. *extract*
A. *Concentrated soil extracts*				
Water	8·9	6	6 (6)	9·0
	8·9	125	110 (–)	9·0
Water (Acidified)	7·2	16	15 (–)	8·9
Alkaline pyrophosphate	7·2	60	10 (–)	10·2
(Acidified)	7·2	83	11 (–)	10·2
Alkaline pyrophosphate	7·2	15	14 (13)	4·1
(Acidified and predialysed)	7·2	26	24 (23)	4·1
Sodium hydroxide	7·2	3	0 (0)	9·0
(Acidified)	7·2	30	6 (2)	9·0
Sodium hydroxide (Predialysed)	7·2	26	18 (–)	2·6
B. 1% *neutral humic acids precipitated from extracts of a fen by:*				
Sodium pyrophosphate	7·0	2	2	1·8
	7·0	40	36	1·8
Sodium fluoride	7·0	2	2	2·0
	7·0	40	37	2·0
Sodium hydroxide	7·0	2	1	2·1
	7·0	40	30	2·1

range when manganese was added to the above extracts and the mixtures were dialysed before electrophoresis. Maine and Schmidt (1935) showed that divalent manganese complexed by various carboxylic acids may occur as cation or as anion depending on the pH value of the solution, but the results obtained here with humic-acid preparations suggest that manganese was held predominantly as a cation over the pH range 4–9.

Dialysis. Table 7 summarizes results of dialysis experiments in which mixtures of increasing amounts of manganese added to various soluble organic-matter fractions and to humic acids were dialysed against

potassium chloride. Water extracts retained about 90 per cent. of their manganese content in a non-dialysable form. While similarly high retention values were obtained when increasing amounts of manganese were added to these extracts, the maximum amounts of manganese thus held varied for extracts of different soils, whose water extracts contained the same amount of oxidizable carbon. The manganese present in

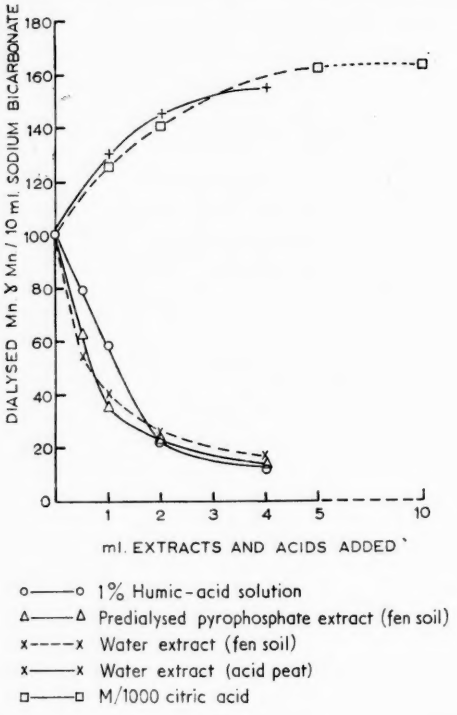

FIG. 1.

alkaline pyrophosphate soil extracts was mostly in a readily dialysable form. If the extracts were first dialysed, the added manganese was retained in a non-dialysable form. Similar results were obtained for acidified sodium hydroxide extracts. The results with humic acids suggested that, independently of the nature of the extracts from which they were precipitated, humic acids could retain some added manganese in a non-dialysable form.

In Fig. 1 the results are set out of dialysing a fixed amount (500γ) of manganese with increasing amounts of various extracts, humic acid, and citric acid in a solution of pH 8·2 and containing 0·02 M sodium bicarbonate and 0·1 M sodium chloride against sodium bicarbonate of the same strength and reaction. Increasing additions of water and pyrophosphate extracts of a fen soil, treated with sodium chloride and

previously extracted with sodium chloride, decreased the dialysable-manganese values in a similar way, despite considerable differences in total nitrogen content. Neutral humic-acid solutions also caused a decrease in the manganese contents of dialysates while additions of either water extract of an acid peat, pre-extracted with sodium chloride, or citric acid, formed dialysable manganese complexes.

Discussion

The distribution of manganese in extracts containing reducing agents of manganiferous soils low in organic matter suggests that manganese higher oxides present or formed in these soils are of the manganese-dioxide type. Since such soils, however, contained only small amounts of divalent manganese and since the trivalent manganese found in neutral pyrophosphate extracts far exceeded twice the amounts of divalent manganese expected from the reverse dismutation reaction, it is possible that at least part of the manganese oxides in these soils occurs as hydrated manganic oxides, as suggested by Dion and Mann (1946). While the results of various extractions, under reducing conditions, of alkaline organic soils prove the absence of difficultly reducible manganese higher oxides, they do not allow any definite conclusions to be drawn with regard to the presence or formation of manganese dioxide in such soils. The recovery values of manganese added as either sulphate or dioxide to alkaline organic soils by alkaline pyrophosphate compared with those obtained by the separate reduction method are consistent with the suggestion that some manganese at least is present in a higher valency form and in combination with the organic matter.

The results of extracting an alkaline fen with ammonium acetate containing copper sulphate confirm that some reduction can take place during these extractions. They do not agree therefore with the suggestion by Hemstock and Low (1953) in regard to the effectiveness of this extractant being due to exchange reaction, but are in full agreement with the findings of Bruun (1945) that the copper contents of water extracts of soils were correlated to their content of organic-matter oxidizable by permanganate. They are also in harmony with the results by Martin and Lavollay (1950) who found that addition of copper salts to humic acids increased the amounts of permanganate needed for oxidation.

The failure by copper salts alone to dissolve various manganese higher oxides as found by Hemstock and Low (1953) agrees with earlier results (Heintze and Mann, 1949) which showed that extraction of manganiferous soils low in organic matter yielded similar amounts of manganese in ammonium acetate with or without added copper sulphate.

The suitability of versenate as an extractant of divalent complexed manganese is in general agreement with Beckwith's results (1955). The complexed divalent manganese constituted generally 10–20 per cent. of the total manganese content of alkaline organic soils. This fraction together with the readily reducible manganese accounted, however, for less than half the total manganese in most of the organic soils, leaving a large part of the manganese present in such soils not determined by the present fractionation. The results of electrophoresis and dialysis

experiments provided additional evidence for the existence of divalent manganese complexed by organic matter of alkaline organic soils as also shown by Beckwith (1955). The present results suggest that the oxidizable carbon or total nitrogen content of soluble organic-matter fractions is not closely related to the capacity of such fractions to retain manganese in a form that is non-dialysable against potassium chloride or sodium bicarbonate. Trocmé *et al.* (1950) concluded from a study of manganese humates that humic acids may assist in maintaining manganese in an exchangeable and therefore available form. The present results show that although manganese added to humic acids may be retained in a cationic form, part of such manganese is retained in a form not dialysable against potassium chloride. The contrasting results obtained by dialysing water extracts subsequent to sodium-chloride extraction of an alkaline fen soil and an acid raw humus peat suggest differences in the nature of the chelating groups of these extracts.

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ESTIMATION OF AVAILABLE NITROGEN FOR ADVISORY PURPOSES IN SOUTHERN RHODESIA

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Summary

In Southern Rhodesia the nitrogen mineralized on laboratory incubation of soil samples taken towards the end of the dry season appears to provide a good index of the nitrogen likely to be available for crop use under field conditions during the subsequent growing season. Incubation for 2 weeks at 35° C., at moistures near field capacity, has been adopted. The occurrence of some soils showing a time-lag between the commencement of ammonification and the commencement of nitrification makes it desirable to determine both ammonia- and nitrate-nitrogen. Owing to practical difficulties in obtaining representative samples of both soil and undecomposed organic matter which has been recently ploughed under, and because it has not been found possible to incorporate this organic matter with the soil sample for incubation in such a way as to reproduce, during the incubation period, its overall effect in the field, soil samples for advisory work are at present sieved before incubation and allowances made for the probable effects of such organic matter when interpreting the results obtained.

The nitrogen mineralized during incubation has been shown to be of the same order as that mineralized in miniature lysimeters maintained in the field under bare-fallow conditions for the duration of the growing season. The mineralized nitrogen obtained after incubation has also been shown to correlate well ($r = +\cdot 83$) with yields, at zero fertilizer-nitrogen levels, of maize and tobacco obtained in the field during seasons of good rainfall.

Responses to fertilizer nitrogen in Rhodesia have been found to be 1–2 bags of maize or 100–200 lb. of tobacco per 10 lb. of nitrogen applied, corresponding to an efficiency of uptake of about 30–60 per cent.

Introduction

In Southern Rhodesia the assessment of nitrogen requirements is of major importance in making fertilizer recommendations, particularly for the two most important crops, tobacco and maize. For both crops the attainable yields are controlled, in the more reliable rainfall areas, predominantly by the supply of available nitrogen, and since very wide variations in soil type and fertility are encountered, a reliable procedure for the prediction of available soil nitrogen would be invaluable; for tobacco, in particular, adjustment of nitrogen supply within fine limits is necessary in order to obtain maximum yields consistent with good quality. During the last three years particular attention has therefore been given to analytical methods of estimating available soil nitrogen in Southern Rhodesia.

As previously reported (Saunder, 1954), it has been possible to establish for different soil conditions relationships between total soil nitrogen and crop yields and to predict the nitrogen-supplying power of soils by a procedure similar to that employed at Missouri (Woodruff, 1949; Smith, 1954). The proportion of the total nitrogen released to tobacco and maize during a cropping season in Southern Rhodesia has been

found on the average to vary from 2 per cent. on red clays to 4 per cent. on sands, but with appreciable variations either way depending on the previous cultural history of the land.

It is apparent that a more direct procedure is to be preferred, particularly where, as in Rhodesia, a wide range of cultural conditions, ranging from newly opened virgin soils to green-manure rotations, is encountered. A suitable incubation procedure such as that developed at Iowa State College (Fitts, Bartholomew, and Heidel, 1955; Stanford and Hanway, 1955; Hanway and Dumenil, 1955; Munson and Stanford, 1955) is more direct and precise, and in the present paper the progress of similar incubation studies in Southern Rhodesia is described.

The Incubation Procedure

1. *Incubation period*

The 2-week incubation period, at the optimum temperature of 35° C. for nitrification, is the same as that favoured at Iowa State College (Munson and Stanford, 1955). It is a convenient period in practice and, as shown in Table 1, much the same relative differences between soils were obtained after incubation for 2 weeks as after longer incubations.

TABLE 1

Nitrifiable Nitrogen after Incubation for Different Periods

Soils (all cultivated—none containing recently incorporated organic matter)	*Nitrate* N *p.p.m.*				
	Initially present	*After 1 weeks' incubation*	*After 2 weeks' incubation*	*After 3 weeks' incubation*	*After 4 weeks' incubation*
Coarse grained sand	8	14	16	17	22
„ „ „	10	20	24	25	32
„ „ loamy sand	17	30	34	37	42
Medium grained sandy loam	3	17	26	28	34
V. fine grained sandy clay	6	22	29	31	39
Red-brown clay	3	22	26	28	33
„ „	7	27	35	39	47
Black clay	10	21	26	27	34

In addition it was found, as shown in Table 5, that the nitrifiable nitrogen released during 2 weeks' incubation is of the same order as that released in miniature lysimeters under field conditions during a cropping season.

2. *Moisture control and aeration*

As found at Iowa (Stanford and Hanway, 1955), the nitrification rate can be greatly increased (sometimes as much as twofold) by mixing the soil with a finely ground vermiculite. It is felt, however, that, particularly on poor structured soils, unduly high figures may sometimes be obtained through supplying better moisture and aeration conditions than are likely to pertain in the field. Some comparative figures for nitrate nitrogen released in incubations carried out with and without vermiculite

and in miniature lysimeters under field conditions are shown in Table 5. In general the nitrifiable-nitrogen figures obtained without vermiculite appear to reflect rather more closely than do those obtained with vermiculite the relative nitrogen-supplying power of the soils as measured in the lysimeters; also nitrification in the presence of vermiculite appears to have been relatively high for three poorly aggregated soils, which are known to have a high nitrogen requirement in the field.

In experiments to determine the optimum moisture for incubation it was found, as shown in Table 2, that within a comparatively wide range of moistures, near field capacity, little variation in nitrate-nitrogen release

TABLE 2

Nitrate Nitrogen Release by Proposed Procedure at Different Moisture Contents

Soil texture	*Nitrate* N (*p.p.m.*) *found after incubation at following moisture levels* (% *by weight*)								
	10%	15%	20%	25%	30%	35%	40%	45%	50%
Coarse grained sand .	13	13	13	8	8	..	..	..	..
„ „ „ . .	22	24	24	24	26	..	..	..	..
Medium grained sandy loam	..	23	26	24	23	16	15	..	..
V. fine grained sandy clay*	..	..	25	29	25	21	0	0	..
Red-brown clay . .	..	..	24	25	26	25	24	25	..
Black clay . . .	..	..	..	22	24	26	23	24	13

* Poorly aggregated soil.

occurred. It was therefore considered that the comparatively simple method of moisture adjustment according to texture, as proposed in this paper, should be satisfactory. In the moisture adjustment a dilute solution of monocalcium phosphate was used in order to rectify possible soil-phosphate deficiencies.

Over a number of determinations no significant differences were found between incubations with flasks that were left open at the mouth and regularly adjusted for moisture losses (which were considerable), and flasks that were kept stoppered with solid cork bungs for the full incubation period, indicating that sufficient oxygen is contained in the flasks for bacterial requirements. It was, however, found that by using a cork bung fitted with a glass tube drawn to a capillary, moisture losses were negligible over 2 weeks in a humid incubator and this procedure was therefore adopted for routine work.

3. *Determination of mineralizable nitrogen*

In the preliminary studies it was found that with very few exceptions conversion of ammonia to nitrate was virtually complete at the end of the incubation period, and it appeared therefore that, as in the Iowa procedures, the determination of nitrate nitrogen only would be sufficient for evaluation of the nitrogen-supplying power of soils. It was also found that in order to obtain, in a single determination, the best picture of the available nitrogen status of the soil, as indicated by maize yields, it

appeared to be somewhat better to include the initial nitrate with the nitrate released during incubation. This was also found by Munson and Stanford (1955) in comparing yields obtained in pot trials with nitrate release on incubation, and is to be anticipated under Rhodesian

TABLE 3

Comparison of Nitrifiable Nitrogen Fractions as Indices of the Nitrogen-supplying Power of a Typical Red-brown Clay

Crop sequence	*Nitrate* N *initially* (*p.p.m.*)	*Nitrate* N *after incubation* (*p.p.m.*)	*Nitrate* N *released during incubation (by difference)* (*p.p.m.*)	*Maize yield (bags/acre)**
1953/4 After maize	6	36	30	14
„ potatoes	8	51	43	20
„ legume green manure	39	87	48	25
1954/5 After maize	4	32	28	10
„ potatoes	21	51	30	26
„ legume green manure	18	64	46	30

* 1 bag = 200 lb. grain.

field conditions where most crops are normally planted with the onset of suitable planting rains after a long dry season. In Table 3 are shown some typical results from a red-brown clay, where the maize yields obtained after different rotation crops compared somewhat better with the sum of the initial nitrate and that released during incubation than with either separately.

The preliminary correlations between field and laboratory data described in the next section were therefore made using the nitrate nitrogen found after incubation as the index of nitrogen-supplying power. A number of soils have, however, now been encountered where little or no nitrate nitrogen is released during the incubation period. The reason for the failure of these soils to nitrify has not been established, but it does not appear to be due to bacterial sterility since inoculation with an infusion from soils of high nitrifying power has proved ineffective. It appears to occur particularly, but not exclusively, with samples taken early in the dry season or from virgin lands; in some cases a further sample taken at a later date is found to nitrify satisfactorily although nitrification is still inhibited in the earlier sample which has been stored in the laboratory.

It has been found that in these soils there is a time-lag between the start of ammonification and the start of nitrification. Some typical examples are shown in Table 4; it will be observed that the 'time-lag' may be quite considerable, and in extreme cases nitrification may still be negligible after 5 weeks' incubation. A similar 'time-lag' has been observed in Australia (Collins, 1954).

In view of the occurrence of such soils in which nitrification is inhibited it is felt that a complete determination of mineralizable nitrogen, including both ammonia and nitrate, should be carried out, and a distillation procedure using Devarda's alloy has been adopted for routine advisory work in Southern Rhodesia.

TABLE 4

Mineralization of Nitrogen on Incubation of some Soils showing Delayed Nitrification

Soil	*Mineralized* N *p.p.m.*							
	Initially		*After 2 weeks' incubation*		*After 4 weeks' incubation*		*After 6 weeks' incubation*	
	NH_3	NO_3	NH_3	NO_3	NH_3	NO_3	NH_3	NO_3
Abnormal soils								
Virgin sandy clay loam .	16	0	42	1	46	1	53	3
Fallowed sand . .	13	0	30	1	32	2	35	5
Rotated sand . .	11	0	27	3	12	19	0	36
Virgin sandy clay loam .	6	0	19	7	4	17	0	28
Virgin sand . .	3	0	6	1	0	9	0	14
Normal soil								
Reverted sand . .	8	0	0	20	0	29	0	38

Laboratory procedure

The following procedure is used for incubating the samples: 10 g. of air-dried 2 mm.-sieved soil are placed in a 100-ml. Erlenmeyer flask and moisture adjustment is made by adding slowly over the whole soil surface a 0·1 per cent. solution of mono-calcium phosphate from a burette. The amount of solution used is: 1·5 ml. for sands; 2·0 ml. for sandy loams; 2·5 ml. for clay loams; 3·0 ml. for kaolinitic red clays and 3·5 ml. for montmorillonitic black clays.

The Erlenmeyer is then stoppered with a cork bung fitted with a glass tube drawn to a capillary and placed in a humid incubator at 35° C. for 2 weeks, during which period germinated weed seeds are removed as necessary.

At the end of the incubation period the samples are analysed as follows:

1. If NO_3 only is required: shake with 40 ml. of a solution of $Ca(OH)_2$, filter, take a suitable aliquot and evaporate to dryness and determine NO_3 with phenoldisulphonic acid.
2. If NO_3 and/or NH_3 are required: shake with 50 ml. of N.KCl/0·1 N.HCl, filter and take suitable aliquots for distillation and determination of ammonia by Nesslerization. In this laboratory the procedure for routine distillation of NH_3+NO_3 together, which is rapid and gives good recovery of N, is to add to a 5-ml. aliquot, in a 100-ml. Erlenmeyer flask, about 0·1 g. NaOH and 0·05 g. Devarda's alloy and then pass steam, which is directed just above the liquid surface, through the flask at such a rate that 25–30 ml. of distillate are collected after 5–6 minutes.

Correlation of Incubation Procedure with Field Data

1. *Relationship to nitrogen release in lysimeters*

During the 1953/4 and 1954/5 seasons a number of miniature lysimeters essentially similar to those described by Taylor and Ellis (1938), consisting of 8–9 in. of soil in tin cans of 7-in. diameter draining directly into Winchester-quart bottles containing thymol as preservative, were filled with different soils and then immersed to soil depth and exposed to normal climatic conditions for the duration of the growing season. The

TABLE 5

Relationship between Nitrate Nitrogen Release on Incubation and in Miniature Lysimeters under Field Conditions over a Cropping Season (Oct./Nov.–March)

Soils	*Initial Nitrate N status (p.p.m.)*	*Nitrate N p.p.m. found*		
		After laboratory incubation		*After cropping season in miniature lysimeters (sum of N in soil and in leachate)*
		Soil alone by proposed procedure	*Soil + vermiculite by modified Iowa procedure**	
1953/4 season				
Rotated granitic sand	6	24	..	23
Red-brown clay from recently ploughed ley	2	16	..	17
Red-brown clay from land under maize	6	36	..	50
Red-brown clay after leguminous green manuring	39	87	..	117
1954/5 season (All samples from rotated lands containing no unrotted bulk organic matter)				
Granitic sand	10	24	25	30
,, ,,	8	16	22	11
,, ,,	9	21	23	20
,, ,,	7	20	34	20
,, loamy sand	17	34	51	34
Sandy loam	3	26	33	28
Red-brown clay. Well aggregated	3	26	43	24
Red-brown clay. Rather poorly aggregated	7	31	64	38
Red-brown clay. Poorly aggregated	7	35	74	31
Grey-brown clay. Very poorly aggregated	6	29	58	20
Black clay. Well aggregated	10	26	36	21

* 10 g. soil and 1·5 g. ground vermiculite were mixed and placed in a Gooch crucible; moisture adjustment was made by suction, but without leaching. Incubation was for 2 weeks in a water-vapour saturated atmosphere.

soils were maintained uncropped and free of weeds; they were lightly cultivated on the surface at intervals to prevent crusting. The leachates were drawn off through the air-vent tube when necessary, without disturbing the soil. Soils were analysed beforehand and soils and leachates at the end of the season, when conversion of ammonia to nitrate was found to have been quantitative. The observed release of nitrate nitrogen is compared in Table 5 with that released on laboratory incubation. It appears that the nitrogen release in the proposed incubation procedure is of the same order as the nitrogen release during a cropping season, at least under bare-fallow conditions.

2. *Relationship to crop yields and uptake of nitrogen*

During the 1952/3, 1953/4, and 1954/5 seasons, which were seasons of favourable rainfall, yields of maize and tobacco in field trials were compared with the nitrate nitrogen found in the soils after laboratory incubation. The maize yields are from trials conducted on a variety of soils (which have been described by Ellis, 1951), ranging from granitic sands to red latosolic clays of widely differing fertility and from many different locations; the yields are from those plots which received adequate phosphate, and in some cases potash, but no nitrogen. The tobacco yields are from trials conducted on granitic sands by the Tobacco Research Board of Rhodesia and Nyasaland; since zero nitrogen treatments were not always included in these trials, yields have in some cases been extrapolated to the zero nitrogen fertilizer level from the nitrogen response curves for the experiment concerned. In all cases soil samples were taken before fertilization and planting. In only one trial was a soil encountered showing inhibited nitrifying power on incubation; the results of this trial have not been used.

The relationship obtained between observed yield and 'nitrifiable' nitrogen is shown in Fig. 1. Considering the variety of soils and localities and the fact that results for three seasons are included, it is felt that the correlation coefficient of 0·83 is remarkably high. It indicates very clearly that in nearly all the trials concerned, in the presence of basic phosphate applications, available nitrogen was the main limiting factor, and suggests that in Rhodesia it is possible to predict likely yields, in good seasons such as those recently experienced, from the mineralized nitrogen obtained after incubation of the soil, as shown by the regression equation in Fig. 1.

The maize yields (in bags/acre) and the tobacco yields (in 100 lb./acre) are plotted on the same scale in approximate accordance with the nitrogen removal of the crops. With hybrid maize it has been found in Southern Rhodesia (Weinmann, 1956) that there is a linear relationship between grain yield and nitrogen removal by the whole crop, a 15-bag (or 3,000-lb.) maize crop removing 45–50 lb. N. The relationship between yield and nitrogen removal has not yet been fully established for tobacco under local conditions; but Parker (1952) states that in N. Carolina a 1,500-lb. flue-cured tobacco crop removes 51 lb. N, whilst preliminary figures obtained by Weinmann (unpublished) indicate that

in Southern Rhodesia the average removal, for a good-quality crop, may be somewhat less.

It is interesting to note that on the basis of these crop removal figures and taking the nitrate nitrogen produced on incubation as being approximately equivalent to the seasonal production of nitrate nitrogen in the field (as shown in Table 5), the average efficiency of use of available soil nitrogen by the maize and tobacco appears to be about 60 per cent.,

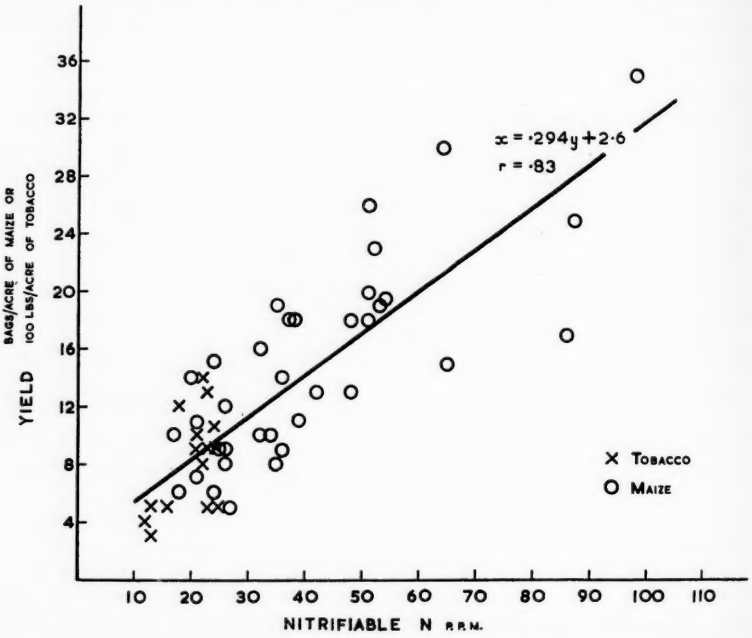

FIG. 1. Relationship between yields of maize and tobacco obtained in field trials (in the absence of applied nitrogen) and the amount of nitrate N produced in soil samples after incubation for 2 weeks at 35°C. The results cover three growing seasons.

assuming crop removal to occur from the top 2,000,000 lb. of soil in an acre. For instance, on a soil providing 42 p.p.m., or 84 lb. per acre, of nitrate N, average yields will be, from the regression line in Fig. 1, 15 bags per acre of maize or 1,500 lb. per acre of tobacco, removing slightly less than 50 lb. N per acre.

It must be emphasized that all the data shown in Fig. 1 were obtained using prepared (i.e. sieved) samples for incubation, and that these samples were taken towards the end of the dry season not long before planting.

Effect of time of sampling

It has been found that as the soil dries out in the field after the rains, an increase often occurs in the amount of mineralizable nitrogen found on incubation. In advisory work, therefore, reliable advice, based on

incubation data, can only be given when samples have been taken after the soil has thoroughly dried out. For samples taken at other times it is often necessary to rely to a greater extent upon the total nitrogen content of the soil in conjunction with its texture and cultural history.

Effects of bulk organic matter

Prior to analysis all samples are passed through a 2 mm. sieve and care is taken to remove, and not to pulverize when crushing soil aggregates, any unrotted organic matter which may be present. The reason for this elimination of bulk organic matter is twofold. Firstly, there are considerable, in fact insuperable, practical difficulties in obtaining, on a routine scale, representative samples of both soil and recently ploughed-under organic matter. Secondly, it has not so far been found possible to include the organic matter in the soil sample for incubation in such a way as to reproduce, during the incubation period, its overall effect in the field. The state of subdivision of this organic matter is of particular importance; if, for instance, it is incorporated in a fine state of subdivision, decomposition is rapid and, with materials of high C/N ratio, microbiological fixation is much more severe than that actually experienced under field conditions.

TABLE 6

Nitrogen Release on Incubation of Prepared Samples taken from a Typical Red-brown Clay which had a Green Manure Crop turned in at the end of March

Sampling date	*Nitrate Nitrogen p.p.m. found in soil*			
	After velvet bean green crop		*After sunhemp green crop*	
	Initially	*After incubation*	*Initially*	*After incubation*
Sampled May (wet) .	28	66	18	71
„ June (moist) .	38	61	34	80
„ July (sl. moist) .	38	68	53	112
„ August (dry) .	37	67	59	120
„ September (dry)	52	81	39	90

Samples prepared in this way are, therefore, used for analysis, and, when interpreting the incubation data, allowances are made for the effects of readily decomposable organic matter which may have been turned in.

With leguminous green manures, which are grown the previous season and turned in towards the end of the rains, it appears that decomposition of the residues is sufficiently rapid for a considerable benefit to be shown in the mineral-nitrogen status of the prepared samples, as illustrated in Table 6. Provided the sample is taken late in the dry season after the soil has thoroughly dried out, it appears that good correlations are still obtained between crop yields and the mineral soil-nitrogen found after incubation, since several of the maize yields shown in Fig. 1 (including

most of those from lands of 'nitrifiable' N greater than 50 p.p.m.) are from leguminously green manured lands.

When non-leguminous plant residues have been incorporated in the soil it appears that allowances for the amount and type of material turned in must be made before attainable crop yields can be quantitatively related to the mineral soil-nitrogen found after incubation. (This is particularly important in Rhodesia in the case of tobacco lands where large amounts of organic matter are often ploughed in.)

If carbonaceous material is turned in late in the dry season, then the nitrogen available to the subsequent crop will be less than indicated by the nitrogen mineralized after incubation of the prepared sample, owing to the organic combination of nitrogen during the decomposition of the unrotted organic matter not represented in the sample. On the other hand, if young and succulent material is turned in early during the previous rains, then a secondary release of nitrogen may be expected for the subsequent crop, as demonstrated by Parbery and Swaby (1942). It appears doubtful whether this secondary nitrogen-release, in contrast to the primary release in the case of leguminous green-manures, will be adequately reflected in short term laboratory incubations, unless decomposition of residues is already largely complete at the time of sampling.

These effects are shown in the case of tobacco in Fig. 1. The results from lands of 'nitrifiable' N less than 15 p.p.m. are from virgin lands ploughed late in the dry season and the observed yields of 300–500 lb. per acre are less than would be predicted from the regression line; whilst three results, where the observed yields of 1,200–1,400 lb. per acre are much greater than would be predicted from the regression line, are from lands which had a millet green crop turned in early before the end of the previous rains.

Tentatively, it appears that, allowing for the efficiency of use of available soil-nitrogen by the crop, the average magnitude of the allowances necessary to make observed yields agree with predictions based on incubation figures is likely to be in accordance with accepted figures for biological fixation of nitrogen by carbonaceous crop residues, or for secondary release of nitrogen turned in in more succulent residues, as found by Parbery and Swaby (loc. cit.).

3. *Assessment of optimum fertilizer nitrogen requirements*

Once it is possible to measure the nitrogen-supplying power of the soil it is possible to predict with greater accuracy the extent to which economic responses to nitrogen fertilization will be obtained.

In Iowa it has been possible to establish correlation curves between nitrogen release on incubation and the optimum nitrogen application required for maize (Hanway and Dumenil, 1955). Insufficient data are as yet available in Southern Rhodesia for the establishment of such curves, and indeed it is doubtful whether climatic conditions can in many areas be considered sufficiently constant for this purpose; but the available data does tend to show that, as in Iowa, the greatest responses to nitrogen are obtained on the soils of poorest nitrogen status. Not only may larger amounts of nitrogen be economically used therefore on the

poorer soils, but on such soils it is also possible to apply greater amounts of nitrogen before the seasonal risk, that is the risk of moisture becoming more limiting than nitrogen, becomes too great.

In practice it appears at present that in Southern Rhodesia, in the better rainfall areas, optimum economic nitrogen dressings vary from over 100 lb. per acre for maize or 40 lb. per acre for tobacco on soils of low nitrogen status (generally analysing 15 p.p.m. mineral N, or less, after incubation) to little or none on soils capable of producing about 30 bags per acre of maize (analysing 90–100 p.p.m. mineral N after incubation) or those capable of producing over 1,600 lb. per acre of tobacco (analysing over 45 p.p.m. mineral N after incubation).

The responses obtained from suitable nitrogen applications on a number of soils of widely differing fertility are shown in Fig. 2. It will

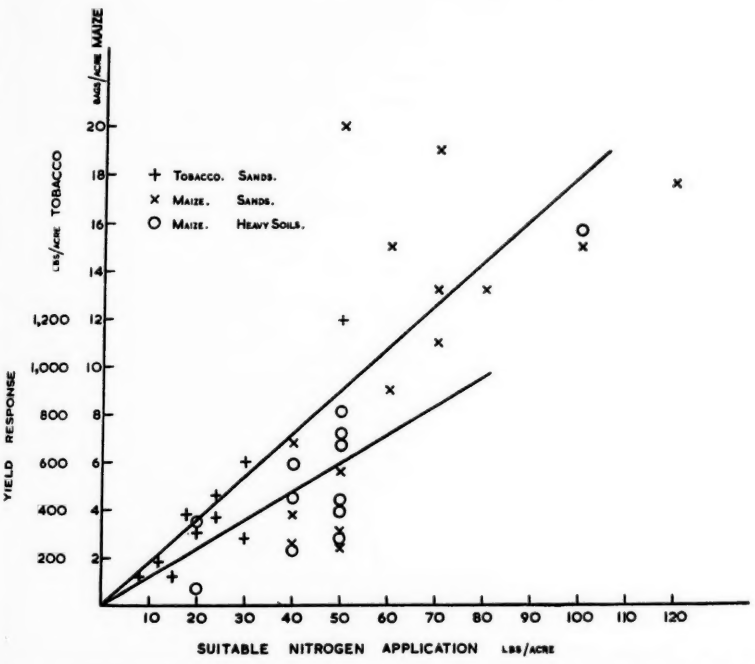

FIG. 2. Response of maize and tobacco to applied nitrogen on different soils. Each point represents the response obtained from a suitable economic nitrogen dressing for the soil concerned. The results cover three growing seasons.

be observed that for practical purposes responses are linear and vary from 1–2 bags of maize or 100–200 lb. of tobacco per 10 lb. of N applied; on the basis of average crop removal figures found in Southern Rhodesia (Weinmann, loc. cit.) this corresponds to an efficiency of use of fertilizer nitrogen of 30–60 per cent.

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THE SOLUBILITY OF MOLYBDENUM IN SIMPLIFIED SYSTEMS AND AQUEOUS SOIL SUSPENSIONS

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Summary

Studies of the precipitation of molybdate by ferric iron and aluminium show that ferric molybdate has minimum solubility at pH 2·7 and that it is less soluble than aluminium molybdate which has minimum solubility at pH 4·8. Ferric molybdate is much less crystalline than aluminium molybdate.

The sorption of molybdate by hydrous ferric oxide, aluminium oxide, and clay minerals depends on pH and the concentration of molybdate in solution. When sorption by the solids is compared, hydrous ferric oxide is outstanding and the order of the others is: aluminium oxide > halloysite > nontronite > kaolinite.

The main process in the sorption studies was probably adsorption of molybdate by anion exchange with hydroxyl ions. Precipitation of aluminium molybdate was detected by X-rays when aluminium oxide and halloysite were treated with concentrated molybdate solutions.

The sorption of molybdate by soils depends on the pH and the concentration of molybdate in solution. A krasnozem which was high in free ferric oxide sorbed the largest quantities of molybdate from solution. Its ability to sorb molybdate was substantially reduced after removing the free ferric oxide by the Mg-oxalate method.

Introduction

THE availability of molybdenum to plants in acidic soils is frequently increased by raising the pH. This relation to pH is analogous to that of phosphate when held in insoluble forms by iron or aluminium and suggests that molybdenum may be similarly held in soils. Although the reactions of phosphate in systems containing iron and aluminium have been studied exhaustively, those of molybdate have received only slight attention. The present work consists of studies of the solubility of molybdate, firstly in simplified systems containing iron and aluminium as metallic chlorides and as simple solids, and secondly in aqueous soil suspensions.

Experiments and Results

(*a*) *Ferric and aluminium molybdates*

A ferric molybdate mineral (ferrimolybdite) has been recognized for some time (Schaller, 1907) and a synthetic ferric molybdate has been obtained by the interaction of ferric chloride and sodium molybdate in acetic acid solution (Carobbi, 1930). While there are no reports of aluminium molybdate, either as a mineral or as a synthetic compound, some preliminary tests in these laboratories showed that a crystalline precipitate of aluminium molybdate could be obtained by the interaction of solutions of aluminium chloride and sodium molybdate. These pieces of information provided the starting-point for more detailed studies of

the mineral ferrimolybdite (Jones and Milne, 1954) and of synthetic iron and aluminium molybdates.

The effect of pH on the solubility of molybdate in systems containing iron and aluminium chlorides was studied first. Solutions of Na_2MoO_4 (0·02 N) were rapidly mixed with equal volumes of either $FeCl_3$ or $AlCl_3$ (0·02 N). HCl or KOH was added to the molybdate solutions before mixing to give suspensions with varying pH. The suspensions were kept at 20° C. and shaken intermittently. After 6 days the pH values of the suspensions were measured and the precipitates were separated by centrifuging. The concentration of molybdenum remaining in solution was determined by the colorimetric-dithiol method (Williams, 1955) using a Hilger 'Spekker' absorptiometer.

The relationship between final pH and the concentration of molybdenum remaining in solution is shown in Fig. 1. The solubility of molybdenum, when bound by aluminium, shows a distinct minimum at pH 4·8. The solubility curve of ferric molybdate has a shape similar to that of aluminium molybdate but its minimum occurs at pH 2·7, at a much lower concentration of molybdenum in solution.

The solubility curves of the ferric and aluminium molybdates are reminiscent of those of ferric and aluminium phosphates (Gaarder, 1930; Teakle, 1928; Perkins, 1948) and ferric and aluminium arsenates (Wiklander and Alvelid, 1950) in that there are minima in solubility in the acidic range. Ferric arsenate has a minimum solubility at pH 2·4 while aluminium arsenate has a minimum at pH 4·1. The data for the phosphates are not in complete agreement, but the minimum for iron phosphate lies between pH 2 and pH 4 while that for aluminium phosphate lies between pH 4 and pH 7. The curves obtained from precipitation experiments depend to some extent on the ratio of phosphate to metal, and although similar relations would probably hold for molybdenum this aspect has not been pursued in the present work.

Ferric and aluminium molybdates which were precipitated close to the points of minimum solubility were analysed for iron,* aluminium,† and molybdenum and examined by X-ray diffraction. The results of the chemical analyses are best expressed as the atomic ratio of molybdenum to metal. This ratio ranges from 1·56 to 1·61 for the ferric molybdates and from 0·48 to 0·51 for the aluminium molybdates. The ratios for the ferric molybdates, which are always higher than that given by the stoichiometric formula $Fe_2(MoO_4)_3$, suggest the formation of polymolybdates. On the other hand, the ratios for the aluminium molybdates are almost constant and suggest a basic salt. Aluminium molybdate is highly hydrated and differential thermal analysis (D.T.A.) reveals that it loses its associated water in three stages; there were endothermic reactions at 120° C., 310° C., and 520° C. It loses 34 per cent. of its weight when heated to 500° C. and a further 17 per cent. when heated to 700° C. The formula $2(Al(H_2O)_4(OH)_2)MoO_4$ would agree with these results.

X-ray powder photographs were taken using a small Phillips powder

* Determined by the colorimetric thioglycollic method.
† Determined by the colorimetric 'aluminon' method.

camera with manganese-filtered iron radiation for the ferric molybdates, and a General Electric camera with nickel-filtered copper radiation for the aluminium molybdates. The powder patterns of the ferric molybdates are very poor and vary slightly, probably with their water content, but

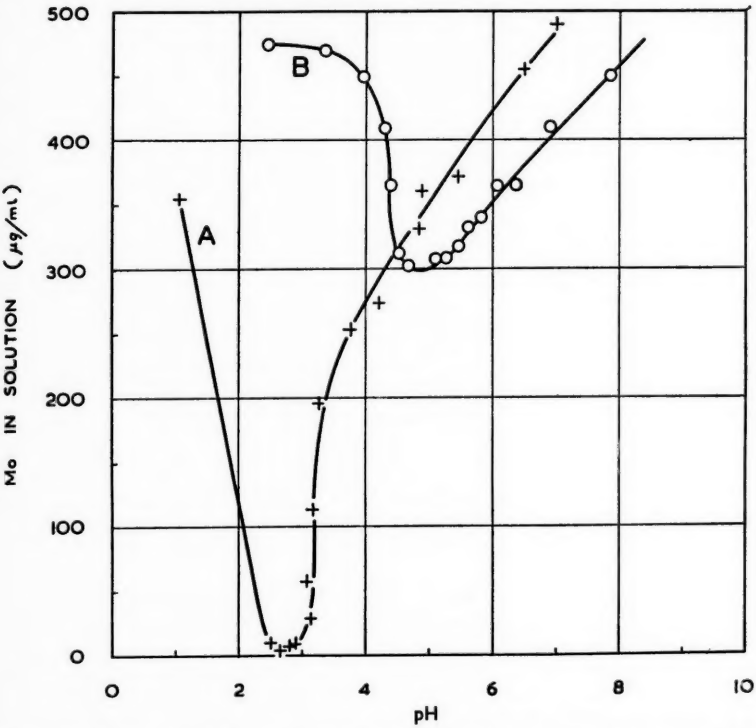

FIG. 1. Solubility of molybdates precipitated with either $FeCl_3$ or $AlCl_3$ at varying pH. A, ferric molybdate; B, aluminium molybdate.

the most consistent spacings have been selected and are shown in Table 1. Only one pattern was given by the aluminium molybdates (Table 1) and this is strikingly well defined when compared with those given by the ferric molybdates.

(*b*) *Sorption* of molybdate by simple solids*

(i) *Description of solids.* The solids selected were hydrous ferric oxide, boehmite, metahalloysite, kaolinite, and nontronite.

Hydrous ferric oxide was prepared by the method of Schuylenborgh and Arens (1950). A solution of 405 g. of $Fe(NO_3)_3 \cdot 9H_2O$ in 1 l. of water was run slowly into a solution of 3·5 M NH_3 in 1 l. of water,

* This term is adopted to mean the removal of molybdate from solution by a solid or soil and has no implications of mechanism.

TABLE 1

Powder Patterns of Ferric and Aluminium Molybdates

Ferric molybdate		*Aluminium molybdate*	
d	*I*	*d*	*I*
9·7	VS	..	..
..	..	9·4	W
8·0	VW	..	..
6·3	W	..	..
5·0	W	..	..
..	..	4·78	VS
4·33	V	..	..
4·12	VW	..	..
3·46	M	..	..
..	..	3·25	VW
3·17	W	..	..
3·07	VW	..	..
2·80	VW	..	..
2·48	W	2·44	M
2·30	VW	..	..
..	..	2·23	S
..	..	1·99	W
..	..	1·74	S
1·63	VW	..	..
..	..	1·46	W
..	..	1·35	VW

VS = very strong, S = strong, M = medium
W = weak, VW = very weak, V = just visible

stirring vigorously all the while. Boehmite was prepared by the method of Schuylenborgh (1951) by adding 820 ml. of 2 M NH_3 to a solution of 50 g. of $AlCl_3$ in 200 ml. of water at a temperature of 18° C. Both precipitates were allowed to settle and washed several times with distilled water by decantation. They were then collected on Buchner funnels and dried at 60° C. for 2 days.

The metahalloysite and nontronite were clay-mineral standards supplied by Ward's Natural Science Establishment Inc., New York. The metahalloysite was sample H-12 from Bedford, Indiana, and the nontronite, sample H33a from Garfield near Spokane, Washington. The kaolinite was a sample of an English Coating Clay.

All solids were ground to pass a 200-mesh I.M.M. sieve and samples were examined by X-ray diffraction. The powder pattern of the ferric oxide showed that it was largely amorphous, but lines of haematite appeared faintly. The pattern of boehmite was diffuse; it was free from bayerite which was a contaminant in the boehmite prepared by Schuylenborgh. The metahalloysite, nontronite, and kaolinite were pure samples.

(ii) *Effect of* pH. The sorption of molybdate by the solids was compared at different pH values. For these experiments the standard procedure was to take 100 mg. of the iron and aluminium oxides and 1,000 g. of the clay minerals. Solutions of Na_2MoO_4 containing 100 μg of molyb-

denum in 20 ml. of water were added to the solid material along with HCl or KOH in another 20 ml. of water to adjust pH. A final 10 ml. of water was added to bring the total volume of solution to 50 ml. The suspensions were shaken for an hour at both the beginning and end of

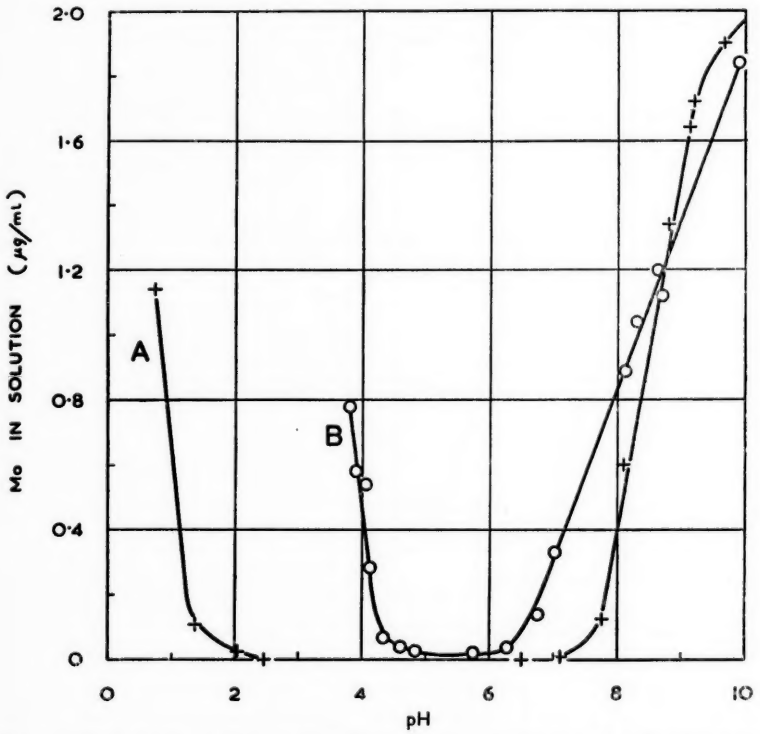

FIG. 2. Effect of pH on the sorption of molybdate. A, ferric oxide, B: aluminium oxide. Mo addition: 100 μg. per 100 mg. solid.

a period totalling 16 hours.* The pH values were then measured and the most acidic suspensions filtered. The less acidic to alkaline suspensions had to be centrifuged at approximately 20,000 g. in order to separate solid material. The concentration of molybdenum remaining in the filtrates and centrifugates was then determined colorimetrically.

The results (Figs. 2 and 3) show that all the solid materials sorb molybdate. Each one shows a maximal sorption on the acid side of neutrality. The relative sorbing abilities of the solids may be most conveniently compared by reading the graphs at, for example, pH 7. Of

* Preliminary experiments showed no differences in the amounts of molybdate sorbed between 16 and 48 hours. A 16-hour period was therefore chosen as a practical approach to final equilibrium.

the sesquioxides, ferric oxide has the greater ability (Fig. 2). Bearing in mind that ten times more solid was used for the clay mineral systems, the relative abilities of the solids may be written: ferric oxide > boehmite > metahalloysite > nontronite > kaolinite.

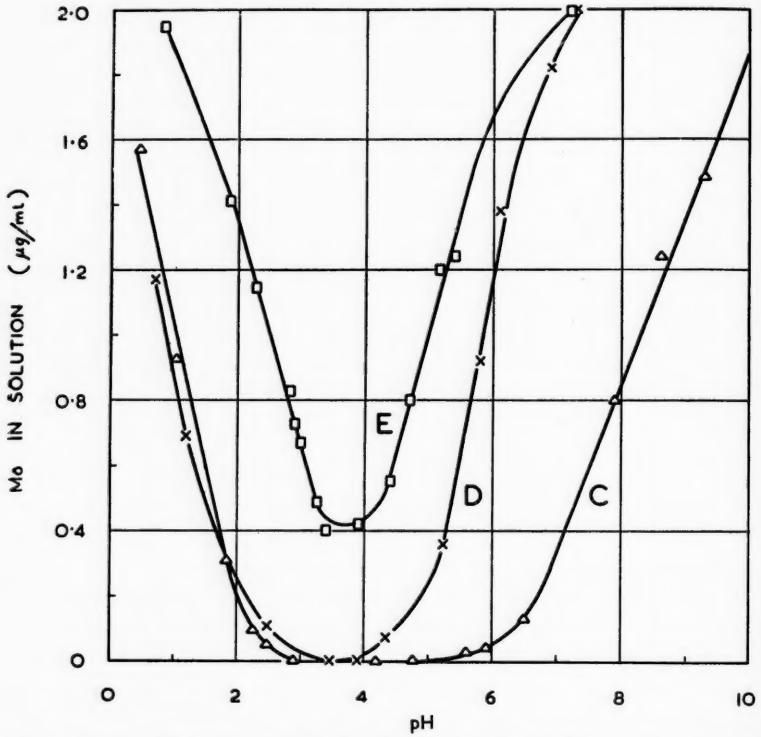

FIG. 3. Effect of pH on the sorption of molybdate. C, metahalloysite; D, nontronite: E, kaolinite. Mo addition: 100 μg. per 1 g. solid.

(iii) *Effect of concentration.* The amount of molybdate sorbed was determined as a function of the final concentration of molybdate in solution at a final pH of 4·35±0·15; the solid phases used were ferric oxide, boehmite and metahalloysite. The experimental methods were as described above except that 100 mg. of each of the solid phases was used and the initial concentrations of both molybdate and HCl were varied.

The results shown in Table 2 give, if plotted, sorption curves which level off at high concentrations of molybdenum in solution. It is better to compare sorption on the basis of equal active areas of the three solids. This may be done by assuming that the levels of sorption reached at the highest concentrations represent saturation of the active areas. The

sorption for a given concentration is then expressed as a percentage of this saturation level and the results so obtained are plotted in Fig. 4. The gradients of the curves show that the solids sorb molybdate in the order: ferric oxide > boehmite > metahalloysite.

TABLE 2

Relation between Molybdenum Sorbed and Final Concentration of Molybdenum in Solution: pH 4·35±0·15

Ferric oxide		*Boehmite*		*Metahalloysite*	
Mo sorbed per unit wt. of solid (*μg./100 mg.*)	*Final concn. of Mo in soln.* (*μg./50 ml.*)	*Mo sorbed per unit wt. of solid* (*μg./100 mg.*)	*Final concn. of Mo in soln.* (*μg./50 ml.*)	*Mo sorbed per unit wt. of solid* (*μg./100 mg.*)	*Final concn. of Mo in soln.* (*μg./50 ml.*)
1,250·0	..	14·6	0·40	17·1	2·88
1,874·9	0·08	24·1	0·85	43·3	6·65
2,499·8	0·16	73·0	2·00	86·4	13·6
3,124·6	0·40	195·7	4·25	130·0	20·0
3,749·4	0·60	294·9	5·12	324·2	50·8
4,373·1	1·92	493·0	7·00	435·0	65·0
4,993·0	7·00	1,237·0	13·0	545·0	80·0
6,226·0	24·0	1,859·0	16·0	640	110
6,949·7	50·3	2,464·9	35·1	720	155
7,410·0*	90·0	3,069·0	56·0	757*	243
..	..	3,658·5	91·5	..	..
..	..	4,225*	150	..	..

* Taken as 100 per cent. saturation.

(iv) *Nature of molybdated solids.* It is important to know whether crystalline molybdates form when ferric oxide, boehmite, and metahalloysite are treated with molybdate solutions. In order to study this, 1 g. samples of ferric oxide and boehmite and 2 g. samples of metahalloysite were separately digested in 50 ml. of sodium molybdate solution (1·00 M) at pH 4·5 to 5·5. Aliquots of 40 ml. of molybdate solution were added along with 10 ml. of HCl to adjust pH values. The suspensions were allowed to stand at 20° C. for 10 days with intermittent shaking. They were then centrifuged and the solid materials were washed thoroughly with water at pH 4·5 and dried at 20° C. Control experiments were carried out in which samples of each of the solids were digested in the absence of molybdate.

All solids were examined by X-ray diffraction. While the powder patterns of the controls were unchanged, the patterns of the treated boehmite and metahalloysite both contained additional reflections, at 4·78 Å and 2·23 Å. These reflections coincide with two of the strongest reflections in the pattern of aluminium molybdate (see Table 1). Since they cannot be attributed to any other material of which the X-ray powder data is known, it appears that crystalline aluminium molybdate was formed. Crystalline aluminium phosphates have been similarly identified when aluminium minerals were digested with concentrated phosphate solutions (Ensminger, 1948; Haseman *et al.*, 1950). No

evidence of ferric molybdate was found in the powder pattern of the ferric oxide treated with molybdate. This is compatible with the extremely poor crystallinity of ferric molybdate and the low solubility of ferric oxide.

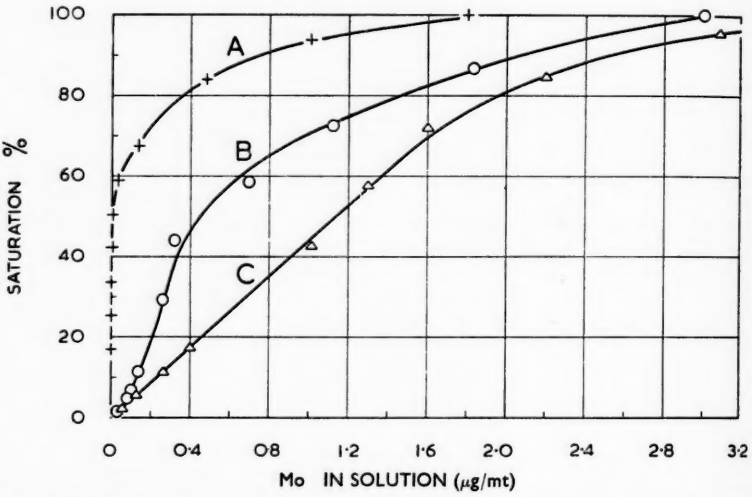

FIG. 4. Relation between degree of saturation of solid and final concentration of molybdenum in solution at pH 4·35±0·15. A, ferric oxide; B, aluminium oxide; C, metahalloysite.

(*c*) *Sorption of molybdate by soils*

(i) *Description of soils.* The studies with simplified systems led to further studies with three soils. These are hereafter referred to by their place names and are as follows:

A krasnozem with pH 5·3 from *Wollongbar* near Lismore in New South Wales: it contains 72 per cent. clay (less than 2 μ), 4·05 per cent. organic carbon,* and 14·9 per cent. free ferric oxide.†

A black clay with pH 7·0 from a reclaimed swamp at *Penola* in the south-east of South Australia: it contains 60 per cent. clay, 4·58 per cent. organic carbon, and 0·2 per cent. free ferric oxide.

A grey gravelly loam with pH 5·9 overlying yellow clay at 10 in. from *Elmhurst* near Ararat in Victoria. It contains 14 per cent. clay, 1·75 per cent. organic carbon, and 1·1 per cent. free ferric oxide.

The inorganic-colloid fractions $< 2\ \mu$ were separated and examined by both X-rays and D.T.A. The Wollongbar colloid consists of metahalloysite, gibbsite, and much poorly crystalline ferric oxide. The

* Determined by the method of Walkley and Black (Piper, 1942) and expressed as per cent. by weight of the air-dry soil.

† Extracted by the method of Jeffries (1946); the results of analyses are expressed as per cent. by weight of the air-dry soil.

metahalloysite was distinguished from kaolinite by D.T.A.; the endothermic peak which occurred at 530° C. was asymmetric and had a slope ratio of 2·8 (Bramão *et al.*, 1952). The poorly crystalline ferric oxide was not detected by D.T.A.; however, abundant haematite was detected by X-ray analysis after the colloid was heated to 500° C. Both Penola and Elmhurst colloids contain illite and kaolinite. There is more illite than kaolinite in the Penola colloid and less illite than kaolinite in the Elmhurst colloid. The kaolinite was identified by its sharp X-ray reflections and also by the symmetric endothermic peak (with a slope ratio of 1·8) which occurred at 560° C. in the D.T.A. trace.

The Wollongbar and Penola soils were chosen because although they both have large amounts of colloid they are respectively high and low in colloidal ferric oxide. The Elmhurst soil was chosen because clover growing on it has shown a spectacular response to molybdenum (Newman, 1955). The cause of this exceptional deficiency is as yet unknown, but the soil serves as an example of a loam low in both colloid and ferric oxide.

(ii) *Effect of* pH. Experiments were designed to compare the ability of the soils to remove molybdate from solutions at different pH values. For these and the later experiments, the soils were air-dried and ground to pass a 2 mm. sieve. Two concentrations of molybdenum in solution were used, namely 1 and 10 p.p.m. For the experiments with 10 p.p.m. of molybdenum, either HCl or KOH in 10 ml. of water was added to 5 g. of soil. Solutions of Na_2MoO_4 containing 500 μg. Mo in 20 ml. of water were then added and finally 20 ml. of water, bringing the total volume of solution to 50 ml. For the experiments with 1 p.p.m. of molybdenum the procedure was similar, except that 20 g. of soil was taken in a total volume of 200 ml. which included either HCl or KOH and 200 μg. Mo. The suspensions were shaken for an hour at both the beginning and end of a period totalling 16 hours. The pH values were then determined and the more acidic suspensions filtered; the less acidic to alkaline suspensions were centrifuged at 25,000 g. for half an hour before filtering. Suitable aliquots were taken for the estimation of molybdenum.

The results are presented in Figs. 5 and 6 where the amount of molybdenum left in 50 ml. of filtrate is plotted against pH. The curves have certain features in common. There are fairly wide ranges of pH in which the soils sorb maximum amounts of molybdate. At the upper ends of these pH ranges there are fairly sharp bends in the curves and with further increases in pH progressively smaller amounts of molybdate are sorbed. The pH values at which these bends occur were raised by decreasing the initial concentration of molybdenum in solution from 10 p.p.m. to 1 p.p.m. With both initial concentrations, however, the bends given by the Wollongbar soil occur at the highest pH values (about 6 and 6·5 respectively) while those given by the Elmhurst soil occur at the lowest pH values (about 3·5 and 4·5 respectively). The difference between the soils may be seen also if the curves are compared at about pH 6. The order in which they sorb molybdate is: Wollongbar > Penola > Elmhurst.

(iii) *Effect of de-ferrating Wollongbar soil.* The free ferric oxide was removed from the Wollongbar soil before measuring the sorption of molybdate at different pH values. This was done on the soil in centrifuge cups by the method of Jeffries. In this method the iron oxide is reduced

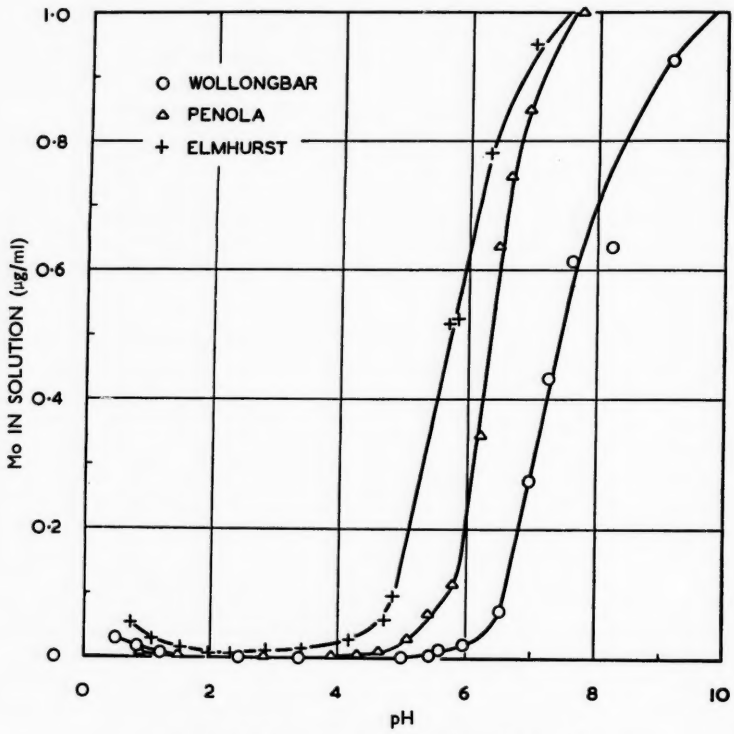

FIG. 5. Effect of pH on the sorption of molybdate by soils.
Mo addition: 200 μg. per 20 g. soil.

by Mg ribbon in a mixture of potassium oxalate and oxalic acid, the iron being then removed in solution. Oxalic acid was removed by washing several times with 0·1 M potassium chloride, and chloride was finally removed by washing several times with distilled water. Each sample was air-dried.

The effect of this treatment on the colloid was examined by both X-rays and D.T.A. For this, a sample of the de-ferrated soil was treated with H_2O_2, dispersed, and the fraction $< 2\ \mu$ separated. Using a standard technique of D.T.A., the trace given by this colloid was identical with that given by the colloid of the original soil. The X-ray powder pattern showed the presence of both a kaolin mineral and gibbsite in the de-ferrated colloid, but haematite was no longer detected

in a sample heated to 500° C. These results indicate that neither metahalloysite nor gibbsite was seriously attacked by Jeffries's method of removing the free ferric oxide.

For the sorption experiments the samples of de-ferrated soil were

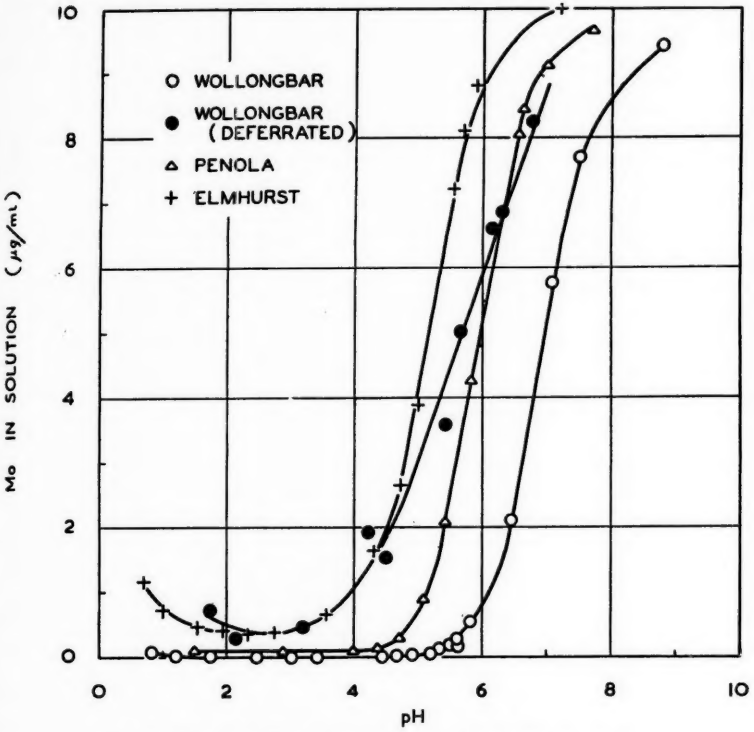

FIG. 6. Effect of pH on the sorption of molybdate by soils.
Mo addition: 500 μg. per 5 g. soil.

shaken in their centrifuge cups with solutions containing 500 μg. Mo in a total volume of 50 ml., the experimental methods being as described previously. The amounts of molybdenum remaining in solution at the various pH values are shown in Fig. 6. Like the untreated soils, this soil sorbed the greatest amounts of molybdate at low pH values and progressively smaller amounts with increasing pH. However, the effect of removing the ferric oxide from the Wollongbar soil was striking; the amounts sorbed were thereby reduced to near those sorbed by the Elmhurst soil.

(iv) *Effect of concentration.* In further experiments the amount of molybdate sorbed was determined as a function of the final concentration of molybdate in solution at a final pH of $4{\cdot}2 \pm 0{\cdot}2$. The experimental methods were similar to those described above except that the

initial concentrations of both molybdate and HCl were varied in the total volume of 50 ml. of solution.

The results (Fig. 7) show that there is some similarity between the curves for the four soils. At first, increasing amounts of molybdate are

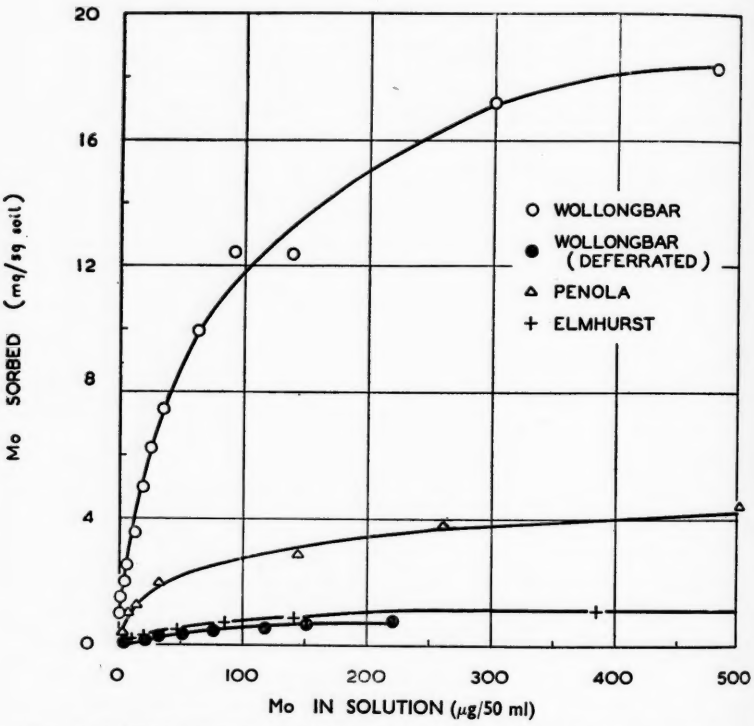

FIG. 7. Relation between sorption and final concentration of molybdenum in solution at pH 4·2±0·2.

sorbed with increasing concentrations in solution. This effect continues until the amounts sorbed by the soils level off. This presumably means that the sorbing components of the soils are becoming saturated. Although the soils are in this respect similar, there are large quantitative differences between them. The Wollongbar soil sorbs much greater amounts of molybdate than the Penola soil, which in turn sorbs more than the Elmhurst soil. These differences are marked, firstly at the lower concentrations of molybdenum in solution, giving large differences in the initial gradients of the curves, and secondly at the higher concentrations where the curves have levelled off. The effect of removing the ferric oxide from the Wollongbar soil is again striking, and the amounts sorbed are lower than those sorbed by the Elmhurst soil.

Discussion

One might expect the behaviour of molybdate to be analogous to that of phosphate and similar to it in complexity. As with phosphate, some workers have emphasized the role of the clay minerals and others that of ferric oxide (Davies, 1956). In the present studies the roles of both clay minerals and sesquioxides have been compared.

Stout *et al.* (1951) and Barshad (1951) have found that molybdate is sorbed by halloysite and kaolinite. From somewhat different experiments they concluded that molybdate was adsorbed by anion exchange with hydroxyl ions. Stout *et al.* showed that hydroxyl ions replaced previously sorbed molybdate, while Barshad showed that the sorption of molybdate was progressively inhibited by raising the pH over the range 5·0 to 9·0. In the present studies, where sorption was measured over a wider range of pH, it was found that both sesquioxides and clay minerals (Figs. 2 and 3 respectively) gave regions of maximum sorption in the moderately acid range. The inhibited sorption found at higher pH values fits in with Barshad's results and leads to the conclusion that hydrous ferric and aluminium oxides also adsorb molybdate by anion exchange with hydroxyl ions.

The experiments at constant pH provide evidence of the importance of ferric oxide. If the curves (Fig. 4) are compared at the lower concentrations of molybdate in solution, the differences in the gradients show that the equilibrium MoO_4^{--} (sorbed) $\rightleftharpoons$ MoO_4^{--} (soln.) is displaced very much farther to the left with ferric oxide than with boehmite or metahalloysite.

It would be interesting to know the mechanisms by which molybdate is sorbed by clay minerals and sesquioxides; or in other words, the relative importance of adsorption and precipitation (which has been widely discussed for phosphate). This distinction has been over emphasized and it is difficult to resolve. What is important is that the same chemical affinities are concerned throughout. If we are to make a distinction, adsorption may be regarded as a chemical reaction of molybdate ions with the cations of the surface without dissolution or disruption of the lattice. This could only occur to the extent of a monolayer. Precipitation, on the other hand, involves dissolution of the cations from the lattice. It must be a slower process than adsorption and was shown to take place in the digestion experiments with concentrated molybdate solutions. In the sorption experiments adsorption was probably the main process. All the results of experiments with simplified systems point to the outstanding affinity of ferric iron for molybdate.

The sorption of molybdate by soils depended on pH and the concentration of molybdate in solution, similarly to the sorption by sesquioxides and clay minerals. The differences in sorption by the Wollongbar, Penola, and Elmhurst soils at a given pH may be related to differences in the total amount of colloid. However, a more definite statement may be made about the role of free ferric oxide. The ability of the Wollongbar soil to sorb molybdate was substantially reduced after its free ferric oxide was removed. This oxide, which accounted for most of the

molybdate sorption, is colloidal and amorphous to X-rays. Its dominating role suports the conclusion that molybdate is more readily sorbed by hydrous ferric oxide than by other constituents of soil colloids. It is of interest to compare the finding by Wells (1956) of a greater affinity of molybdenum for iron than for aluminium. While ironstone nodules contained 10 p.p.m. of molybdenum, aluminous nodules contained less than 1 p.p.m.

The agronomic principle that lime makes molybdenum more available fits neatly into the principle that is here discussed, namely that the molybdate ion is adsorbed by ferric oxide and is exchangeable with hydroxyl ions. This principle seems to have been frequently implied, and Williams and Moore (1952) have actually related availability to the iron content and pH of soils. From the results of chemical analyses of plants and soils they arrived at an equation of the form: $\log Mo \equiv a.pH - b.Fe + c$, where the iron was that dissolved by boiling the soil with 6N hydrochloric acid.

The work by Wells (1956) contains substantial information on the availability of molybdenum to plants. The best agreement between his work and the principle discussed here is seen in the studies of the soils derived from greywacke. As these soils increase in age the amount of free sesquioxides increases and with this the sorption of molybdate increases. At the same time the uptake of molybdenum by plants decreases. This simple picture is unfortunately complicated by his account of the soils derived from basalt. One would expect the availability of a given amount of molybdate to increase as the crystallinity of the sesquioxides increased. Wells however says the opposite and quotes the surprising result in which the soils with the highest sorption power grew plants with the greatest content of molybdenum.

It is unfortunate that the problem of availability has been confused by some who have emphasized the role of ironstone to the exclusion of the more important fine-earth fraction.

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